ADVANCED NO_x CONTROL ASSESSMENT

Prepared for

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FOREWORD

This work was performed as a task assignment under the FGC Environmental Program, Subtask 5.01. Participants in the preparation of this report include:

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ADVANCED NO_x CONTROL ASSESSMENT

1. INTRODUCTION AND SUMMARY

1.1 Purpose of Project

The purpose of this project is to review and assess the current status of commercial and advanced flue gas NO_x control technologies for utility and large industrial boiler applications in support of PETC's program development for the Proof-of Concept Test and Evaluation of Advanced NO_x Control Processes. Emphasis has been placed on the following areas:

- o Understanding the current status of advanced technologies and their potential applicability;
- o Qualitative assessment of technology advantages and disadvantages;
- o Identification of data gaps and poorly understood phenomena;
- o Identification of recent significant technology advances; and
- o Strategic use of various technologies.

Each technology (or group of similar technologies) is evaluated in a separate section of the report. A general overview of a technology is initially provided, followed by a specific review of key technology operating mechanisms, components, materials, systems integration, etc. Results are provided from recent test programs sponsored by DOE and others. Large-scale design configurations are quantitatively examined (if sufficient data was available). R&D considerations and recommendations are provided. In addition, a technology assessment data sheet has been completed for all technologies reviewed; a blank form is shown in Figure 1-1. These data sheets can be updated on a regular basis and can be compiled into a separate quick reference resource.

The remainder of Section 1 briefly examines the broad-based NO_x emissions issues and their impact on control technology, reviews the current control regulations in Germany and Japan and their overall approach to NO_x control, assesses the need for more advanced NO_x control technology, reviews the utility boiler NO_x control market characteristics and examines key aspects of integrated NO_x control technologies and implementation strategies.

1.2 Major NO_x Emissions Issues

Recent research findings link nitrogen oxides (NO, NO_2 and N_2O, collectively called NO_x) to a broad range of air pollution problems, including acid deposition, the atmospheric production of photochemical ozone (the brownish haze in the air commonly called smog), health-

FIGURE 1-1

Sample NO_x Control Technology Review Form

TECHNOLOGY NAME:

TECHNOLOGY TYPE:

EMISSIONS CONTROLLED:

TECHNOLOGY DESCRIPTION:

PREVIOUS PETC EVALUATION UPDATE:

TECHNOLOGY APPLICABILITY:

DEVELOPMENTAL STATUS:

RAW MATERIALS, UTILITIES:

BY-PRODUCTS PRODUCED:

TECHNOLOGY ADVANTAGES & DISADVANTAGES:

ADVANTAGES	DISADVANTAGES

TECHNOLOGY NAME:

CRITICAL DATA GAPS/POORLY UNDERSTOOD PHENOMENA:

RECENT DEVELOPMENTAL ADVANCES:

KEY TECHNOLOGY SUPPLIERS:

threatening nitrate particles that also limit visibility and the formation of toxic nitrogen compounds, such as nitrosamines. Faced with such health and acid precipitation problems, several countries, such as Japan and West Germany, have adopted very strict boiler NO_x emission control regulations which necessitate the application of add-on control technologies to both existing and new industrial and utility fossil-fired boilers. While combustion modifications (i.e. low-NO_x burners) clearly represent the most cost-effective NO_x control techniques (if they can be utilized), the high reduction levels required by the new regulations have "forced" the boiler operators in Germany and Japan to also install high-efficiency flue gas NO_x control technologies. Coal-fired facilities represent the greatest control challenge due to their higher NO_x generation potential and the added difficulties brought about by the significant generation of other pollutants, such as SO_2, SO_3 and fly ash.

1.2.1 Current Role of NOx Emissions on Acid Rain Phenomenon & Ozone Formation

Atmospheric nitrogen oxide (NO_x) compounds primarily include NO, NO_2, N_2O and the nitrate ion (NO_3^-). They can have direct effects on the environment or play a role in the formation of secondary compounds, such as ozone and nitric acid (HNO_3). Recent data presented by NAPAP indicates that the growth in NO_x emissions has slowed substantially[1], although total NO_x emissions have doubled since the end of World War II. NO_x, in the form of nitric acid, typically contributes about 33% of the free acidity in precipitation in industrialized areas, while sulfate contributes about 60%. Roughly one-third of the anthropogenic NO_x emissions come from utilities, one-third from industrial sources and one-third from transportation vehicles.

There is no simple, direct relationship between ambient NO_x concentrations and ozone concentrations[1]. Ozone can be destroyed by reaction with NO, but also formed by further reactions with NO_2 and hydrocarbon free radicals. Average ozone concentrations are relatively uniform across the U.S. with few variations in the annual average by more than 30%. It is highly interesting to note that some recent atmospheric models have shown that reductions in NO_x formation can actually lead to higher levels of ozone concentrations on a local basis[2]; this can occur in situations where a reduction in NO_x concentration yields in a high ratio of volatile organic compounds (VOC's) to NO_x. High VOC/NO_x ratios favor ozone formation. Thus in urban environments, NO_x reduction-alone will have uncertain impacts on ambient ozone concentrations. Besides ozone, complex nitrate compounds can be formed which contribute to photochemical smog.

This past Summer's pollution problems are likely to add greater pressure for tighter emission controls; more than 24 urban areas suffered high levels of smog and ozone and many areas registered more violations of federal ozone standards in the first half of 1988 than during all of 1987.

1.2.2 Effects of NO_x on Health

Pulmonary disfunction is likely to be the most prevalent effect on human health by NO_x. Current results of EPRI's Health Studies Program indicates that NO_2 alone may not be responsible for lung disfunction among individuals who already suffer from pulmonary disease and asthmatic tendencies. Some other "unidentified component of photochemical smog" may be a contributing factor in conjunction with NO_2.

1.2.3 Effects of NO_x on Forests

It is very important to note that recent experimental work indicates that the pollutants which may be responsible for acidifying lakes and streams in North America and Europe are probably not the same agents that are damaging forests in those same regions. The implications of this statement are not at all clear-cut, but Dr. Robert Bruck of the University of North Carolina has pointed the finger of guilt at NOx, rather than SO_2, in terms of forest damage[3]. Additionally, he has made it clear that "dozens of other potentially harmful compounds" (other than SO_2 and NO_x) may also play an important role.

NO_x has been previously been implicated in forest damage through its role in contributing to the formation of acidic precipitation and ozone which can destroy cell membranes in leaves and needles, as well as mobilize toxic aluminum in surrounding soils. Additionally, a recent theory suggests that trees may be receiving too much nitrogen at the end of the growing season which prevents them from being fully prepared to deal with winter temperatures, subsequently suffering frost and desiccation damage. In reality, multiple stresses appear to be involved which can affect different tree species in different ways and the same species differently at different locations. There is also evidence that forest declines have occurred in the past and may be a part of a larger cycle of forest behavior that is neither recognized nor understood. Few U.S. forest studies have been designed to test the hypotheses regarding cause and effects of atmospheric acid deposition.

There appears to be some correlation between areas of forest damage and higher than normal concentrations of heavy metals, such as lead, in surrounding soils. While there is evidence that lead, for example, can impact soil microbial activities, there is no hard evidence that ambient levels of metals participate in tree mortality. However, it is important to observe that areas with significant heavy metals accumulation, probably are indicative of areas in which high anthropogenic pollution deposition is occurring. Thus surface soil heavy metal contamination, particularly down wind of a pollution source, may be indicators of atmospheric deposition fluxes taking place within a region.

NAPAP's interim assessment of the causes and effects of acid deposition concluded the following with regards to the impact of NO_x on forests[4]:

- Nitrogen oxides do not adversely affect U.S. forests on a regional scale. Concentrations of NO_x are typically much too low to produce visible foliar damage.

- There is currently no direct evidence that the combination of SO_2 and NO_x causes forest decline, even at relatively high levels of both.

- There is no synergistic negative affect resulting from simultaneous exposure to trees by NO_x and ozone.

- Combinations of SO_2, NO_x and ozone do not produce a synergistic impact on trees. Ozone is the key gas causing tree damage.

1.2.4 Effects of NO_x on Climate

N_2O may be the key NO_x constituent to affect the earth's climate. N_2O has been determined to be the third most important non-CO_2 "greenhouse" gas (behind methane and fluorocarbon-11). It has an atmospheric concentration of about 310 ppb and an estimated atmospheric lifetime of 150 years[1]. (In contrast, CO_2 has an atmospheric concentration of 345 ppm). Its overall contribution to the greenhouse effect is currently less than 10%; the historic growth rate in N_2O concentration correlates closely with growth in the use of fossil fuels, particularly coal and fuel oil. The N_2O growth rate is reported to be between 0.18 and 0.26 percent per year[1]. One source of data claims that about 31% of total N_2O emissions are due to fossil fuel combustion and biomass burning; however, it appears that there is considerable uncertainty regarding the contribution of anthropogenic N_2O emissions due to the use of nitrogenous fertilizers and to deforestation.

A number of analytical models have been created to predict the build-up of greenhouse gases in the atmosphere[5]. The various scenarios investigated suggest growth rates for NO_2 ranging between 0.05 percent per year to 0.56 percent per year. Thus in the year 2050, NO_2 concentrations are likely to range between 360 and 470 ppbv. Some of these models assume that N_2O will increase at a rate equal to the annual rate of growth in coal combustion.

N_2O has been implicated as a possible contributor to the 30% ozone concentration depletion observed over the South Pole in the Antarctic spring. This phenomenon has been observed since the late 1970's and appears to be increasing in size and magnitude. N_2O is stable enough to reach the stratosphere, where it is photo-dissociated to release free nitrogen atoms which can enter into catalytic chain reactions which destroy ozone molecules. Stratospheric ozone acts as a shield that prevents the most harmful ultraviolet radiation from penetrating to the earth's surface.

As discussed above, N_2O is also a radiatively active trace gas which absorbs infrared radiation reflected from the earth's surface (greenhouse effect). Models indicate that increases in N_2O at historically observed rates will increase the average atmospheric temperature by 0.1°C by the year 2030[5]. The same models predict a total temperature rise of 1.5-5°C.

A key question that must be answered is whether fossil fuel combustion directly contributes significant quantities of N_2O to the atmosphere. Previous N_2O emissions data from fossil fuel combustors have indicated stack emissions on the order of 100 ppm. Recent testing sponsored by DOE (AR&TD), EPA and EPRI directly contradicts past measurements of N_2O generation in combustion systems[6,7]; on-line measurements from a number full-scale utility boilers (coal- and oil-fired), along with laboratory and pilot-scale experiments, measured direct N_2O emissions of less than 5 ppm. N_2O emissions could not be correlated with the NO_x levels in the flue gas. Past miscalculations of combustion N_2O appear to stem from a "sampling artifact" whereby N_2O is produced in sampling containers waiting to be analyzed; the production mechanism is dependent on the initial concentration of NO and the amounts of SO_2 and water present in the sampling container.

These recent tests indicate that N_2O is primarily being indirectly produced in the atmosphere after the release of NO_x from various sources. Greater understanding of the pertinent atmospheric chemistry will be needed to determine the most effective way of limiting N_2O generation.

1.2.5 Impact of NO_x on Vegetation

Independently, NO_x compounds do not yield significant damage to vegetation unless concentrations are much higher than ambient levels; low concentrations of NO_2 are sometimes beneficial. However, the combinations of ambient levels of ozone, SO_2 and NO_2 (50 to 100 parts per billion) have been shown to produce deleterious impacts on vegetation[4]. It is claimed that significant economic benefit associated with crop gains (billions of dollars) would come as a result of a 25% reduction of ozone levels.

1.2.6 Impact of NO_x on the Acidification of Aquatic Systems

The Environmental Defense Fund (EDF) recently completed a study on acidification of coastal waters that attributes the problem to emissions from coal-fired plants. However, EDF scientists indicated, for example, that nitrogen compounds responsible for "choking" aquatic life in the Chesapeake Bay were from local sources, especially motor vehicles, pesticides and other sources apparently not linked to coal. The report has been criticized for lack of detailed analysis of the polluting nitrogen compounds.

Acidification of lakes and streams has been of major concern in the U.S. since the acid rain phenomena was identified. Nitric acid is currently of less concern than sulfuric acid due to its lesser contribution to precipitation acidity. Lake acidification models, indicate less response to the nitric acid, not only because of their lower amounts in acid rain, but because the aquatic watershed typically has natural sinks (trees and other plant life) for nitrogen which limits the total amount of nitric acid entering a lake or stream[2].

1.3 Current NO_x Control Regulations in U.S., Germany & Japan

Three countries, the United States, Japan and most recently West Germany, have been most influential in the development of NO_x control regulations, being the first of the industrialized countries to institute such limits and the most progressive in updating their regulations as new environmental facts have emerged. Since the early 1970's the United States has recognized the need to control NO_x emissions; with the passage of the 1970 Clean Air Act new source performance standards (NSPS), the Environmental Protection Agency limited the amount of NO_x that could be generated by new coal-fired utility and industrial boilers larger than 73 MWt to 0.7 lb/MMBtu (860 mg/Nm^3). This regulation was revised by the 1977 Clean Air Act Amendments to yield limits ranging between 0.5 lb/MMBtu (625 mg/Nm^3) for subbituminous coals to 0.6 lb/MMBtu (750 mg/Nm^3) for other coals. In November of 1988, the U.S. joined a new international protocol under the United Nations Economic Commission for Europe's Convention on Long Range Transboundary Air Pollution, which provides for an agreement to limit NO_x emission levels. The agreement, known as the "NO_x Protocol," requires the 34 countries that signed it to freeze their NO_x emissions, beginning in the mid-1990's, at levels achieved in 1987 or "any other previous year." The agreement obligates the signers to apply best available control technology (BACT) to stationary and mobile sources to achieve the desired NO_x levels.

The first governmental NO_x regulations were set in Japan in 1973 and have been revised five times, with the most recent revision occurring in 1983. Until March 1987, the national emissions limit is set at 0.5 lb/MMBtu (616 mg/Nm^3). Following March 1987, the NO_x limit will be lowered to the equivalent of 0.33 lb/MMBtu (410 mg/Nm^3) for plants greater in size than 210 MW(e) and 0.42 lb/MMBtu (513 mg/Nm^3) for plants ranging between 34 MW(e) to 210 MW(e)[8]. However, in Japan local regulations take precedence over the federal standards, since local regulatory agencies typically want lower emissions. The usual procedure is for a utility to negotiate with the local group when a new unit is planned to determine the actual allowed emissions (in terms of volume/day)[9]. As an example, the agreed upon local limit for the Electric Power Development Company's Takehara Unit 1 is set at approximately 0.12 lb/MMBtu (150 mg/Nm^3)[10].

In 1983 West Germany enacted a major acid rain control directive which set comprehensive emission standards for both new and existing facilities above 50 MWt. The primary reason for these regulations was a result of the extensive forest damage, considered to be tied to air pollution, which has occurred in some regions of the country. Effects on trees has been particularly severe in the area of North Rhine-Westphalia in the central portion of the country, as well as in Baden-Weurttemberg in the southwest. The 1983 legislation was revised in 1984 by an accord among federal and provincial environmental ministers to substantially reduce the original limits set for NO_x control. The existing coal-fired boilers (with future operation of unrestricted duration) as well as all new boilers must limit NO_x emissions to 0.16 lb/MMBtu (200 mg/Nm^3). Table 1-1 provides a detailed list of the current West German regulations[10]. At the same time, the accord called for control deadlines to be set by the individual provincial jurisdictions. Not surprisingly, the state government of Baden-Weurttemberg was the first to impose prompt

TABLE 1-1

RECENT NOX CONTROL REGULATIONS FOR WEST GERMAN COAL-FIRED BOILERS

Boiler Type	NO_x Emission Limit, lb/MMBtu (mg/Nm^3) (6% O_2 Basis, Dry Bottom; 5% O_2 Basis, Wet Bottom)	
Size, MW(e)	18 to 110	Over 110
New Units, Dry Bottom:		
1983 Limits	0.65 (800)	0.65 (800)
1984 Limits[1]	**0.33 (400)**	**0.16 (200)**
New Units, Wet Bottom:		
1983 Limits	1.46 (1800)	1.46 (1800)
1984 Limits[2]	**0.33 (400)**	**0.16 (200)**
Existing Units, Dry Bottom:		
1983 Limits	1.06 (1300)	1.06 (1300)
1984 Limits[1]	**0.53 (650)**	**0.16 (200)**
Existing Units, Wet Bottom:		
1983 Limits	1.63 (2000)	1.63 (2000)
1984 Limits[2]	**1.06 (1300)**	**0.16 (200)**

Notes

1. Must be implemented as early as possible or by 1988 in Baden-Wuerttemberg and North Rhine-Westphalia

2. Must be implemented as early as possible or by 1990 in Baden-Wuerttemberg and North Rhine-Westphalia

deadlines; dry bottom boilers, both new and existing must comply by 1988 and wet bottom boilers by 1990[11]. Similar deadlines have also been established by other state jurisdictions, including North Rhine-Westphalia. It is expected that the retrofit program on existing West German boilers larger than 110 MW(e) will be completed by 1990, resulting in an average of 70% reduction in NO_x emissions. Surveillance of NO_x emissions by continuous monitoring and recording of stack NO is required for coal and oil-fired boilers larger than 18 MW(e). NO_x control compliance requires that all daily mean values be equal or smaller than the emission limit requirement; 97% of half-hour mean values must be equal to or smaller than 1.2 times the emission limitation and all half-hour mean values must be equal to or smaller than twice the emission limit[12].

1.3.1 NO_x Control in Japan & Germany

As detailed above, both Japan, and more recently, Germany have had to contend with more stringent NO_x control regulations which has forced them to make the difficult decisions regarding the selection of control technologies. In Japan, the selective catalytic treatment of boiler flue gas is currently the preferred technology for achieving high levels of NO_x reduction from boiler flue gas. This is primarily a direct result of the concerted R&D effort by the Japanese to develop emissions control processes to try to meet their original stringent 1973 ambient limits (0.02 ppm on a daily basis) and associated boiler emission control standards. Through 1985 the SCR technology has been applied to about 170 boilers in Japan, with two-thirds of these being utility applications; approximately 20% of the latter have been retrofits for coal-fired plants[13]. The total installed SCR capacity now exceeds 30,000 MW(e). It is important to note the general practice is to precede the SCR with a high degree of combustion modification, since the latter is usually considerably less expensive. Since most of the Japanese SCR experience is with comparatively new, base-loaded oil-fired boilers, the direct transfer of their technology and experience to coal-fired applications in other countries must be accompanied by appropriate test programs.

Widespread application of Japanese SCR technology is now occurring in West Germany due to passage of extremely stringent NO_x control regulations in 1984 for new and existing coal-fired boilers, as discussed previously. The 200 mg/Nm^3 requirement for boilers larger than 110 MW(e) surpasses NO_x control requirements in all other nations including Japan. This emission limit is well beyond the capabilities of combustion modification techniques and, therefore, also requires the use of flue gas cleaning technologies. Due to the early deadlines (late-1980's) for compliance in West Germany, the highly developed SCR process is being most broadly evaluated and applied, even though other advanced processes have the combined capability to reduce both SO_x and NO_x. However, due to concerns about the applicability of the Japanese SCR technology to existing facilities, over 50 SCR pilot-plant trains have been installed and tested to assess catalyst performance and characteristics[14]. These extensive field, pilot-scale investigations are taking place because the German boilers to be retrofitted with the SCR technology are considered to have a more variable load pattern (more frequent load swings) than those similarly equipped Japanese plants; such operation may effect process control, performance and could physically degrade the catalyst structure due to thermal shock. In addition, the possible unique effects of the fly ash from German coals is of concern. The results of these tests are just now being utilized in the initial commercial installations.

Most of the current West German NO_x control installations are occurring in Baden-Wuerttemberg, the most heavily forest-damaged area, and North Rhine-Westphalia, which is the greatest emitting area. In the former, 3700 MW(e) of SCR will be in place by 1990. The first major SCR facility has been installed on a 460 MW(e) bituminous coal-fired, dry bottom boiler and began operation in early 1986. Another installation (160 MW(e) capacity) on a bituminous-coal-fired, wet-bottom boiler will achieve close to 90% NO_x removal. Approximately 30,000 MW(e) of large boiler capacity will be controlled in North Rhine-Westphalia by 1989 or 1990. In total, the boiler NO_x emission inventory throughout West Germany will ultimately be reduced by 1.5 million tons, principally by SCR[15]. Six of the ten competing SCR process suppliers in Germany are licensees of Japanese processes, three offer German developments including use of activated lignite coke, ceramic molecular sieve, and iron oxide and an American licensor, Norton, uses a zeolite-type catalyst. Currently publicized sales of SCR systems in West Germany for initial startup during the 1986-1988 time period are listed in reference 16. One of the more unique approaches to SCR being evaluated by Germany is the adaptation of rotary regenerative air preheaters to incorporate catalyst-coated plates so as to serve as an SCR reactor. The basic concept is based on the fact that regenerative heat exchangers have a surface area comparable in size to that of a typical SCR reactor; therefore, why not integrate the catalyst into the heating surface of the already installed unit and avoid the need for a separate SCR reactor[17]. Another unique SCR development revolves around the use of lignite coke as an inexpensive SCR catalyst[18].

Combustion modification is playing a major role in Germany for industrial boilers smaller than 110 MW(e) because of its comparatively low cost and less stringent regulations. However, few existing coal-fired utility boilers have yet to be retrofitted with low-NO_x combustion systems. New boilers are being equipped with newly-developed low-NO_x burners[12].

A full-scale test of a wet, absorption-reduction process by Lurgi/Saarberg-Holter (at the Hayden Station in Germany) for combined NO_x/SO_x removal has turned into a significant failure. The complexity of such a process is likely to have been the primary contributing factor[19].

1.4 Acid Rain Legislation's Impact on Potential U.S. NO_x Control

This past June marked what could be the eventual compromise that yields acid rain legislation, especially with the retirement of Senate Majority Leader Byrd of West Virginia. The compromise legislation, reached between Governor Celeste of Ohio and Governor Cuomo of New York, is written to balance the concerns of the coal-burning Midwest with that of the Northeast, the region of the nation most impacted by acidification.

In terms of NO_x reduction requirements, the proposed legislation calls for NO_x emissions to be reduced by 25% by 1998 (approximately 3 million tons annually), including an allowance for mobile source reductions. A key aspect of the legislation, which may be introduced as amendments to the Clean Air Act, calls for spending $2.5 billion dollars by the government over a 10-year period to develop appropriate pollution control equipment to burn coal cleanly; no funds will be provided for coal switching. Power plants and industrial boilers are primarily targeted by the plan to reduce NO_x. Each state would be required to submit a NO_x reduction plan, for reducing NO_x generated within its borders, by 1993.

Both DOE and EPRI have criticized any acid rain legislation as counter-productive to the purposes of the Clean Coal Technology program. Both are strongly pushing the clean coal technologies as the long-term solution to SO_x and NO_x pollution. American Electric Power, one of the countries largest investor-owned utilities and dependent on coal for about 80% of its fuel mix, recently threatened to cancel its planned 330 MW, $579 million PFBC repowering retrofit at its Sporn generating unit if acid rain legislation is passed.

1.5 Need for NO_x Control

Current evidence implicates NO_x (and combinations of NO_x with other gaseous compounds) as a major environmental pollutant. An effective pollution reduction program should account not only for SO_2 control, <u>but also for NOx</u> and fine particulates.

Current U.S. legislation controlling NO_x emissions can, for the most part, easily be met by current design practice and combustion modifications. Projected acid rain legislation is calling for relatively modest NO_x reductions (3 million tons annually). Since a significant portion of the pre-NSPS utility boilers are suitable for combustion modification retrofit, it is likely that low-NO_x burners and other combustion modification methods would suffice. Tightening of NSPS to lower emission levels will not come until the 1990's; specific changes will likely depend on the next administration in Washington. Under the most likely circumstances, SO_x control will continue to be the primary focus.

However, while significant NO_x controls are not on the immediate horizon, steps must be taken now to insure that U.S. utilities and industry have the technological base to achieve significant NO_x reductions should the political/legislative environment change significantly (and it may). Germany has been forced to primarily adopt expensive Japanese SCR technology for its utility boilers to meet their restrictive emissions constraints and reduction deadlines. While costs have been dropping for this technology, it is still very expensive compared to combustion modification and results in secondary pollution (gaseous ammonia and fly-ash/ammonia). Additionally, even the SCR technology has not been rigorously tested for U.S. high sulfur coal applications. Like Germany, the U.S. could be forced to <u>import</u> technology and expertise to deal with stricter pollution control regulations.

There is a clear need to develop alternative, low-cost NO_x control technologies for the U.S. boiler market. While alternative coal combustion systems, such as FBC and gasification/combined cycles, represent technologies which integrate pollution control directly into the system, they may not, in the long run, be as cost-effective as current technology combined with advanced control systems. It is still too early in the game to forsake existing coal combustion technology for which there has been amassed much knowledge and experience. In any case, the significant retrofit market is reason enough to proceed with advanced concepts; R&D dollars expended to devise such concepts are extremely small compared to the billions that may have to be spent to retrofit existing technology.

1.6 Overview of NO_x Control Technologies

Figure 1-2 summarizes the current commercial and advanced NO_x control technology arsenal; the technologies have been segregated into four different areas to highlight their manner of application. The commercialized technologies immediately available to utilities and industry are low-NO_x burners (for most boiler types with the exception of cyclone burners), operational combustion modifications (except reburning), Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR) for low-sulfur coal applications. Low-NO_x burners, for retrofit and new applications, are designed to replace original burner designs so as to distribute fuel and air in such a way as to minimize their mixing at critical NO_x formation temperatures. All of the major boiler manufacturers have developed low-NO_x-burners for their particular furnace designs. NO_x reductions from uncontrolled boilers range between 40 - 70% depending on site specific and operational conditions; typically no more than a 50% reduction will be achieved. Previous BRSC/SAIC NO_x control reviews in 1985 and 1987 have covered these in detail[13,14].

While low-NO_x burners can be considered hardware combustion modification, operational combustion modifications can also be applied separately or in conjunction with low-NO_x burners. All of the techniques listed in Figure 1-2 are available and can be applied on a site-specific basis, except for the advanced reburning concept. All are designed to more carefully control furnace fuel/air mixing, temperature, and combustion chemistry. NO_x reduction efficiencies up to 50% are most likely. These technologies have also been discussed in previous technology updates and the reburning technology was discussed in detail in reference 15.

The flue gas NO_x control technologies identified in Figure 1-2 are of primary interest in this report. These technologies have been divided into two areas to clarify the fact that some technologies dissociate NO_x or convert it to other disposable forms, while others under investigation separate the NO_x from the flue gas and concentrate it for further processing. Figure 1-3 further subdivides the flue gas NO_x control technologies into nine areas of alternative technology-types and identifies specific processes currently under active R&D; most of the R&D in the U.S. is being sponsored by DOE. Most of these technologies are discussed in detail in this report as described in Section 1.1. Table

FIGURE 1-2
GENERAL COMBUSTOR/BOILER NOx CONTROL METHODS

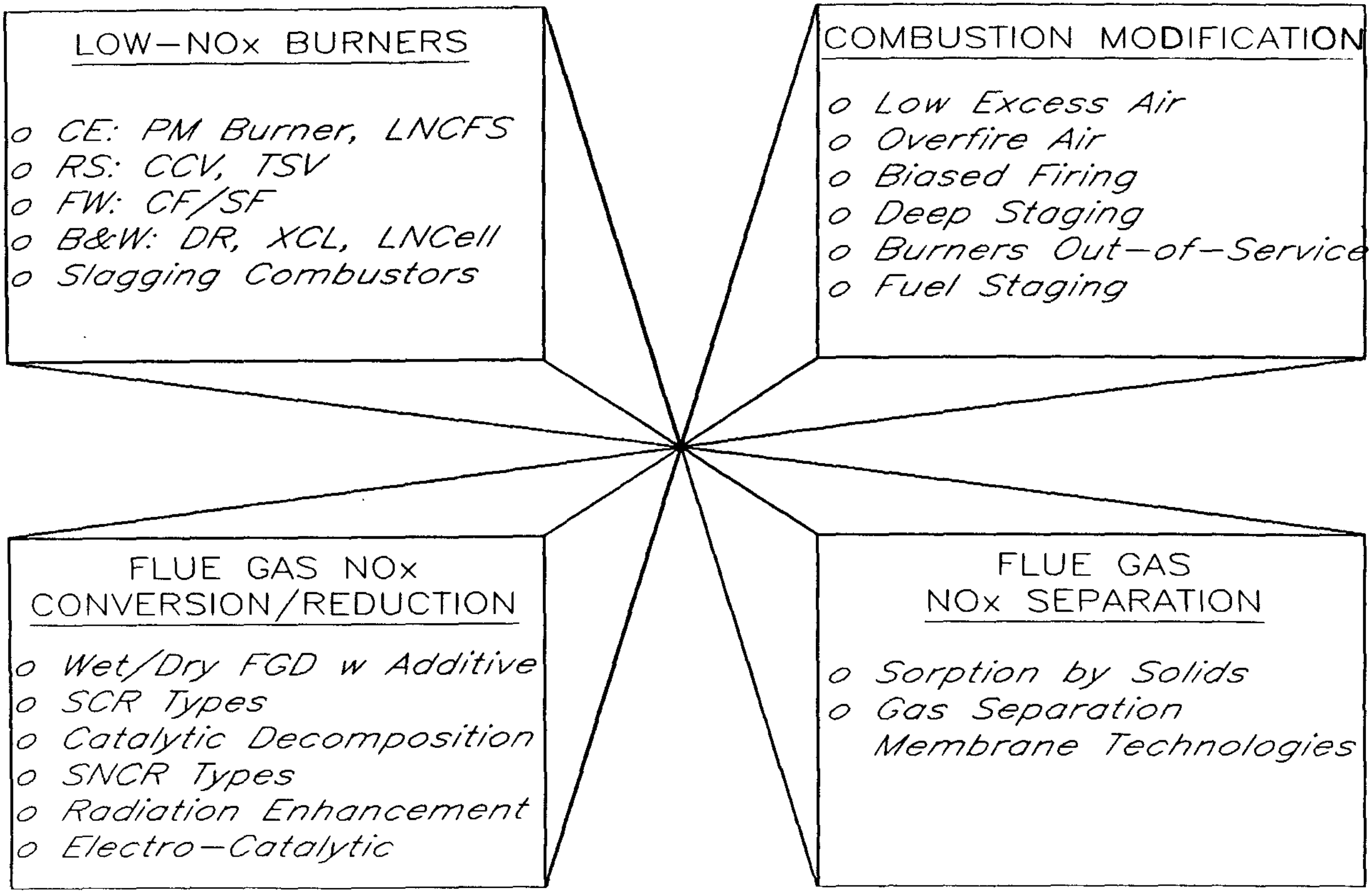
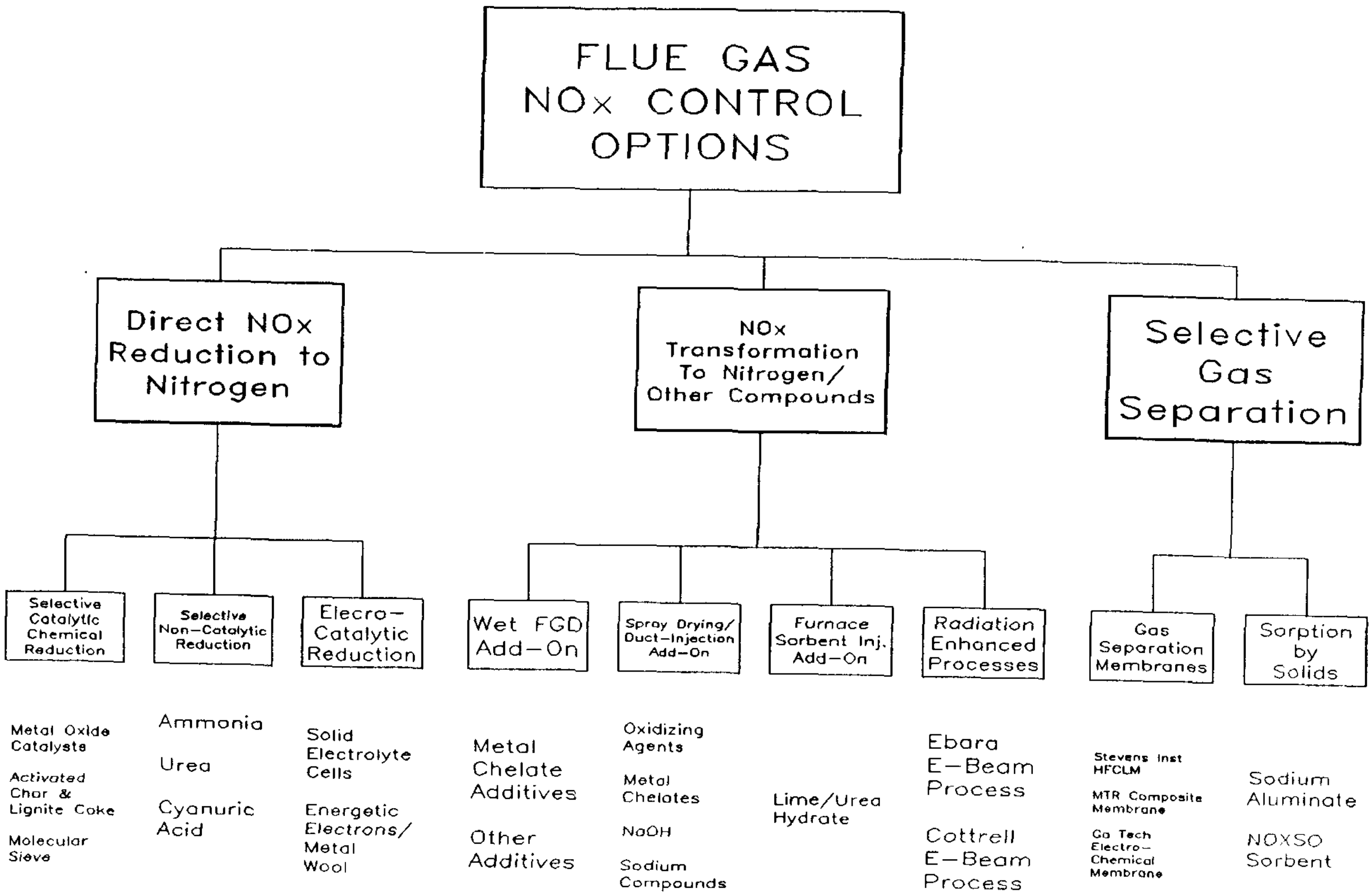


FIGURE 1-3
ADVANCED FLUE GAS DENITRIFICATION TECHNOLOGIES



1-2 summarizes some of the key aspects of these technologies and identifies the section of this report in which they are reviewed. The final part of this introductory section examines the strategic implications for applying these technologies.

1.7 Strategies for Developing/Utilizing NO_x Control Technologies

As in the case of FGD technologies, the key controlling factors affecting the implementation of NO_x control technologies are 1) the applicable environmental control regulations, 2) the emissions control implementation schedule and 3) the cost/benefit associated with the application of each technology (annual cost per ton of pollutant eliminated) that is commercially available. The first dictates the control levels that must be attained (by law) and the second factor constrains the "polluter" to a certain time-table to achieve that control. In the case of Germany's gaseous emissions clean-up program, the first two factors have, for the most part, dictated that a high efficiency flue gas control technology be used. The state of today's NO_x control technology has, therefore, given the decided advantage to the Japanese SCR technologies. However, the SCR technologies are very expensive, from a cost/benefit perspective, when compared with commercial FGD technologies. Depending on the degree of NO_x removal required, the application size and the initial NO_x concentration in the flue gas, SCR can roughly cost between \$3000 - \$6000 per ton of NO_x reduced. Additionally, the significant drop in the dollar versus the yen has made Japanese SCR catalysts considerably more expensive to purchase. Of course, U.S. catalyst manufacturers, such as Norton, may be able to deliver an equivalent catalyst product at a lower cost than the Japanese.

The initial premise of this strategic evaluation must be that NO_x regulations will tighten significantly (similar to that of Japan and Germany), but that the time constraints for implementation will permit the development of alternative technologies (or improved technologies) suitable for our applications that are more cost-effective than existing technology. What are our applications? Currently, retrofit applications represent the clearest market for control technologies. While repowering with advanced, low-emission combustion systems has great technical potential and can be considered the "competition", comparative economics will ultimately determine how wide-spread will be its use. The advanced combustion technologies will be much more formidable competition in the "new" boiler market which, while currently stagnant, will have to increase significantly in the 1990's in order to meet increased power demand at the turn of the century and beyond. While the new boiler market is unclear, advanced control technologies may give new life to existing boiler technology.

1.7.1 Utility Boiler NO_x Control Market Characterization

Power generation units that came on-line in the ten years prior to the implementation of the NSPS regulations represent the largest fraction of the national NO_x emissions emitted by utility boilers (2.5 million tons per year). This is shown in Figure 1-4. Justification for examining NO_x

TABLE 1-2
FLUE GAS NO_x CONTROL TECHNOLOGY OVERVIEW

TECHNOLOGY TYPE/ R&D ORGANIZATION	KEY TECHNOLOGY OPERATING PRINCIPLES	TECHNOLOGY R&D STATUS	KEY CONSUMABLES	KEY BY-PRODUCTS	POTENTIAL NOx REMOVAL	REPORT CROSS-REFERENCE, TECHNOLOGY DATA TABLE
Direct NO_x Reduction to Nitrogen						
Selective Catalytic Reduction (SCR)/ **Many developers/vendors**	Metal oxides catalyze the reduction of NO_x by ammonia injection	Commercial for low-sulfur coal applications, high sulfur applications to be tested in U.S.	NH_3, steam, electricity	Nitrogen, gaseous NH_3 emissions, NH_3 salts, fly ash with NH_3, spent catalyst	70 - 90%+	Section 2, Table 2-12
Selective Non-Catalytic Reduction (SNCR)/ **Exxon - NH_3 inj. Emcotec - proprietary Fuel Tech - Urea inj. KVB - Urea Inj.**	Reducing agent injection into upper furnace where high temperatures ensure fast chemical kinetics - no catalysts needed	Many commercial industrial boiler applications, large-scale testing taking place in Germany	NH_3 or Urea or cyanuric acid or proprietary hydrocarbons	Nitrogen, gaseous NH_3 emissions, NH_3 salts, fly ash with NH_3	70 - 90%	Section 3, Table 3-1
Electro-Catalytic Reduction - Solid Electrolyte Decomposition Cells/ **Ceramatec - zirconia IGR/Helipump - proprietary**	Solid electrolyte of stabilized zirconia or stabilized ceria directly reduce NO_x and transfer O_2 to cell anode	Bench-scale testing for several years	Electricity	Nitrogen, oxygen	Uncertain for practical application, should be high	Section 4, Table 4-1
Electro-Catalytic Reduction - Energetic electrons on metal wool catalyst/ **U. of New Hampshire**	Energetic electrons induced on surface of metal wool catalyst contact colliding NOx molecules which dissociate	Bench-scale testing just initiated	Electricity	Nitrogen, oxygen	Uncertain for practical applications	Section 5, Table 5-1
NO_x Transformation to Nitrogen/Other Compounds						
Electron-Beam Processes/ **Ebara - NH_3 injection Research Cottrell - Combined with lime spray dryer ENEL (Italy)**	Electron guns used to produce oxidizing radicals (OH, HO_2 & O) in flue gas to yield nitric and sulfuric acid fumes which react with appropriate reagent	Pilot-scale testing completed, future depends on developers	NH_3 or lime, power, water	Ebara: Ammonium sulfate-Nitrate mixtures Cottrell: Calcium sulfate, calcium nitrate	90% - SO_x 70-90% - NO_x	Not evaluated

TABLE 1-2 (Continued)
FLUE GAS NO_x CONTROL TECHNOLOGY OVERVIEW

TECHNOLOGY TYPE/ R&D ORGANIZATION	KEY TECHNOLOGY OPERATING PRINCIPLES	TECHNOLOGY R&D STATUS	KEY CONSUMABLES	KEY BY-PRODUCTS	POTENTIAL NOx REMOVAL	REPORT CROSS-REFERENCE, TECHNOLOGY DATA TABLE
Wet FGD Processes with metal chelate additives/ANL, DOW Chemical, PETC, Japanese Processes, LBL	Metal chelate addition to conventional wet scrubber chemistry promotes the enhanced solubility of NO and form nitrosyl metal chelates which react with absorbed SO_2 to produce reduced nitrogen species	Pilot and full-scale tests of some processes	Metal Chelating agents, water, power, SO_2 reagents	Nitrogen, Nitrogen-sulfur compounds	70-80% - NO_x 90% - SO_x	Section 8, Table 8-1
Lime-based Dry Scrubbing with additives/ANL, PETC, U. of Tennessee, U. of Texas, Niro	Additives to lime spray drying and other dry scrubbing systems promote the oxidation of NO_x and formation of calcium-nitrogen and sulfur-nitrogen compounds	Pilot and large-scale tests have been performed with NaOH additive. Other additives tested at bench-scale.	NaOH (or other additives), water, power, lime	$CaSO_4$, $CaSO_3$, $Ca(NO_3)_2$, $Ca(NO_2)_2$, Nitrogen	70-90% - SO_x 40-70% - NO_x	Section 6, Table 6-1
Gas Separation Technologies						
Gas Separation Membranes/ MTR - composite membrane, Stevens Tech - Hollow fiber contained liquid membrane (HFCLM)	Partial pressure differential across the appropriate membranes can selectively remove NO_x (& SO_x) from flue gas	Bench-scale tests, in the R&D cycle	Power, make-up membrane fluids	Concentrated NO and SO_2	Unknown, SO_2 selectivity has been much better than for NO_x	Section 7, Table 7-1
Sorption by Solids/ NOXSO Process	Uses Alumina substrate coated with Na_2CO_3 as sorbent to adsorb SO_x & NO_x. Chemical and thermal regeneration yields concentrated NO_x and SO_x.	Tested at PETC's 500 lb/hr coal-fired boiler, 5 MW proof-of-concept unit is being designed.	Sorbent, power, natural gas or other reducing gas	Conc. NO_x, sulfur or sulfuric acid	90% - SO_2 80 - 90% - NO_x	Not evaluated
Electro-Chemical Membrane/ GA Tech	Electrolyte-containing membrane between two porous, gas diffusion electrodes: applied voltage drop drives the removal of SO_x & NO_x at the cathode and concentration at the anode	Bench-scale tests over several years, preliminary economics are positive, NO_x control needs further work, but may be in doubt	Power, concentrated SO_2	Oleum ($H_2S_2O_7$),	Unknown	Not evaluated

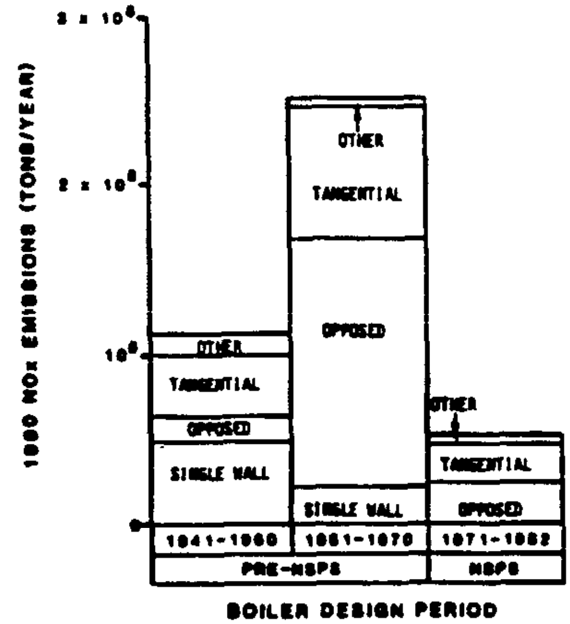


FIGURE 1-4. DISTRIBUTION OF ANNUAL NOx EMISSIONS BY DESIGN PERIOD AND FIRING ARRANGEMENT.

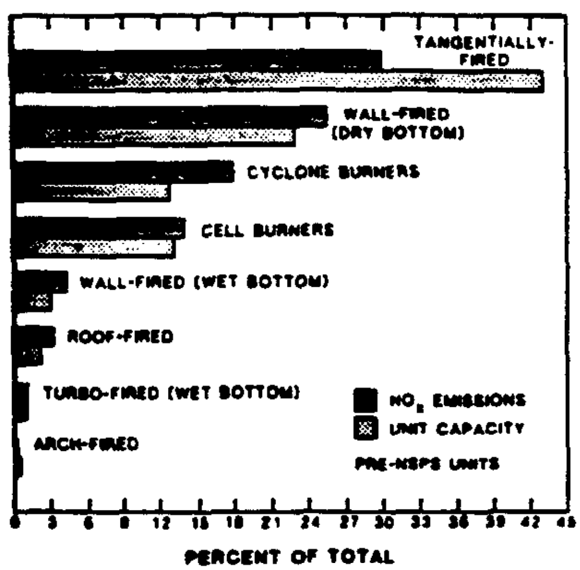


FIGURE 1-5. COMPARISON OF TOTAL NOx EMISSIONS AND UNIT CAPACITY

retrofit options for existing boilers is clear in that pre-NSPS emissions for the period 1941 - 1970 are 5 times that of the post-NSPS boilers. Large pre-NSPS units (greater than 600 MW) represent only 23% of the coal-fired boiler population, but this is equivalent to almost 40% of the installed capacity, which presents a significant opportunity to optimize the number of control installations to achieve large NO_x reductions. Figure 1-5 compares total NO_x emissions and unit capacity of the pre-NSPS boilers; as shown the wall-fired (dry bottom) units, cyclone units and cell burner units have NO_x emissions that are disproportionately larger than their installed capacity.

EPRI studies have shown that, at least, 60% of the coal-fired NO_x emissions (from 100 MW boilers and greater) could be considered as candidates for some form of low-NO_x burner retrofit as shown in Figure 1-6. However, more detailed investigation of site-specific factors indicates that only about 38% of the pre-NSPS coal-fired boiler capacity could be retrofitted with low-NO_x burners (see Table 1-3); thus only about 25% of the total boiler population can readily be retrofitted with commercial low-NO_x burners. Based on the above information, the conclusion must be drawn that a significant opportunity exists for other combustion modification techniques (e.g. reburning) and flue gas treatment technologies. A significant advantage of the flue gas treatment approach is the avoidance of dealing with the complex boiler, burner and fuel-type interactions which impact combustion modification. There is also no need to be concerned with the potential material impacts of low-NO_x combustion modification on boiler internals; reduced boiler life because of material corrosion could be considered as a "hidden" cost associated with such technologies. Flue gas treatment potentially offers the greatest NO_x control with the least impact on boiler control and operability over the operable load range.

Other boiler market characteristics, besides the applicability of combustion controls, can have a significant impact on potential NO_x control development and implementation strategies. These are:

- Existing FGD processes & process-types;
- Boiler SO_x/NO_x emissions;
- Boiler particulate control technology (ESP vs. fabric filter);
- FGD processes under development for acid rain control; and
- Market for recovered products/waste disposal needs.

Conversion of existing FGD systems for combined SO_x/NO_x control is a NO_x control method that has considerable appeal due to the already large installed FGD base and the potential systems that may have to be installed because of long-awaited acid rain legislation. Table 1-4 summarizes the current installed (and planned) capacity of utility FGD systems[16]; total controlled capacity that is operational or under construction is over 66,000 MW. Table 1-5 categorizes the FGD process

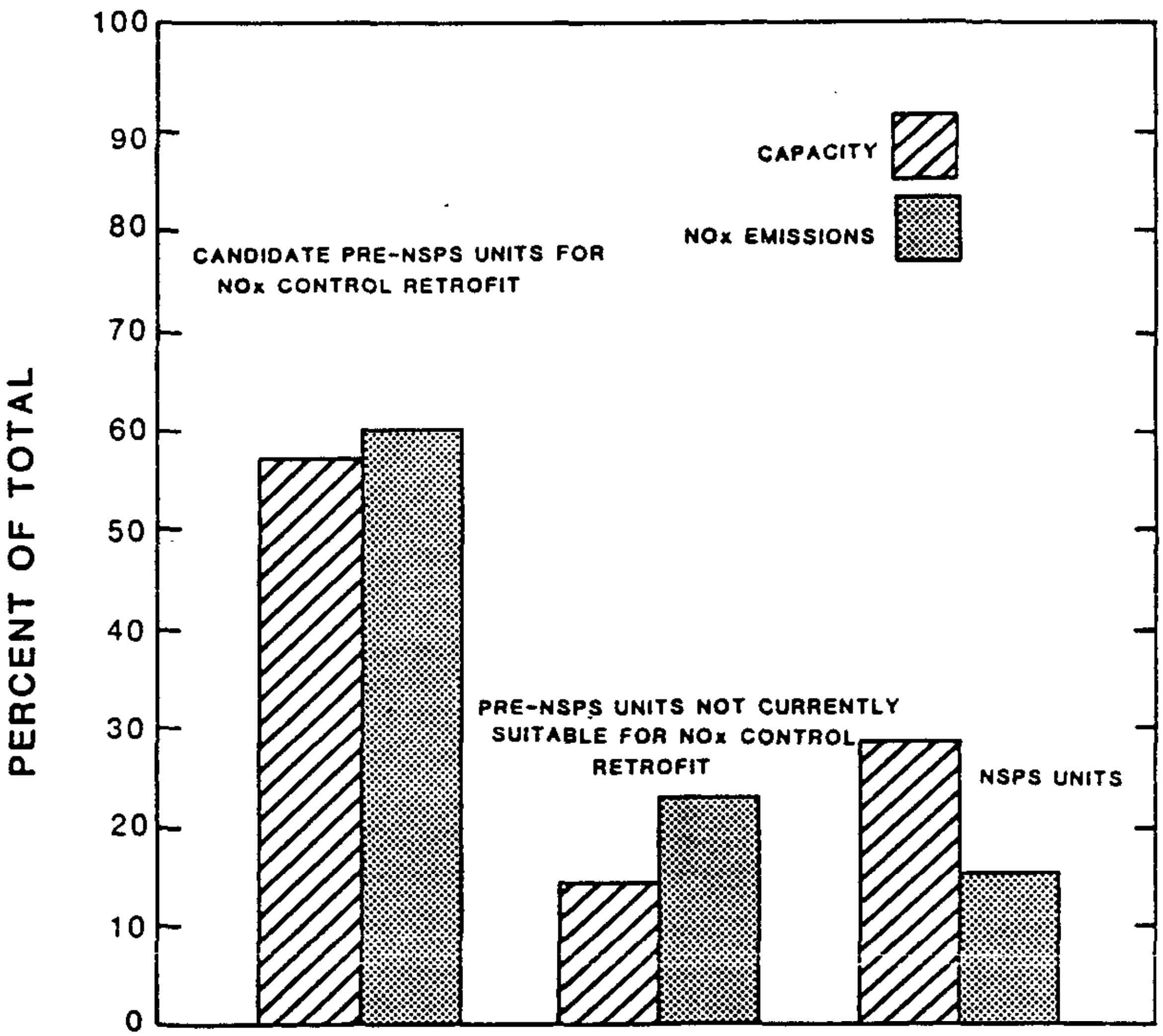


Figure 1-6. Coal-Fired Utility Boilers NO_x Retrofit Potential

Note: Data include only units over 100 MW.

TABLE 1-3

PRELIMINARY ESTIMATES OF COMMERCIAL LOW-NO_x BURNER RETROFITABILITY FOR COAL-FIRED BOILERS

Boiler Category	Capacity (MW)	% of Total Capacity	Boilers Suitable for Low-NO_x Burner Retrofit %	Capacity
Pre-NSPS Boilers				
CE Tangential	75,958	31	50	37,979
B&W Cell-Burner	24,501	10	-0-	-0-
Cyclone Boilers	23,392	9	-0-	-0-
B&W Wall-Fired w/ Circular Burners	16,280	6	70	11,396
F/W Wall-Fired	15,737	6	70	11,016
R/S Wall-Fired	8,283	3	80	6,626
Wet Bottom Wall-Fired	4,917	2	-0-	-0-
Roof-Fired	3,839	2	-0-	-0-
R/S Turbo-Fired	1,988	1	-0-	-0-
Miscellaneous	1,926	1	-0-	-0-
Pre-NSPS Subtotal	176,821	71		67,017
Post-NSPS Boilers				
CE Tangential	30,247	12		
B&W Wall-Fired	21,291	8		
F/W Wall-Fired	12,276	5		
R/S Turbo-Fired	7,138	3		
Post-NSPS Subtotal	70,952	29		
TOTAL	247,773	100		

TABLE 1-4

NUMBER AND INSTALLED CAPACITY OF UTILITY FGD SYSTEMS

Status	No. of units	Total controlled capacity, MW*	Equivalent scrubbed capacity, MW†
Operational	135	57,899	54,229
Under construction	15	8,320	8,054
Planned:			
Contract awarded	13	9,261	9,261
Letter of intent	2	1,780	1,780
Requesting/evaluating bids	0	0	0
Considering only FGD systems	41	22,948	22,363
TOTAL	206	100,208	95,687

* Summation of the gross unit capacities brought into compliance by the use of FGD systems regardless of the percentage of the flue gas scrubbed by the FGD system(s).

† Summation of the effective scrubbed flue gas in equivalent MW, based on the percentage of flue gas scrubbed by the FGD system(s).

TABLE 1-5

SUMMARY OF FGD PROCESS DESIGN

	Operational		Under construction		Contract awarded		Total	
	No.	MW*	No.	MW*	No.	MW*	No.	MW*
Throwaway product								
Wet								
Nonregenerable								
Limestone	60	26,008	9	5,564	8	5,405	77	36,977
Lime	39	17,113	-	-	2	2,036	41	19,149
Sodium carbonate	6	1,505	1	550	2	1,100	9	3,155
Regenerable								
Dual alkali	5	1,963	1	265	-	-	6	2,228
Dry (nonregenerable)								
Lime	12	3,893	3	1,510	1	720	16	6,123
Sodium carbonate	1	440	-	-	-	-	1	440
Salable product								
Wet								
Nonregenerable								
Limestone	2	624	1	165	-	-	3	789
Regenerable								
Wellman Lord	7	1,959	-	-	-	-	7	1,959
Magnesium oxide	3	724	-	-	-	-	3	724
TOTAL THROWAWAY PRODUCT	123	50,922	14	7,889	13	9,261	150	68,072
TOTAL SALABLE PRODUCT	12	3,307	1	165	-	-	13	3,472
TOTAL WET	122	49,896	12	6,544	12	8,541	146	64,981
TOTAL DRY	13	4,333	3	1,510	1	720	17	6,563
TOTAL NONREGENERABLE	120	49,583	14	7,789	13	9,261	147	66,633
TOTAL REGENERABLE	15	4,646	1	265	-	-	16	4,911

* Scrubbed capacity

types being applied; limestone and lime throwaway FGD systems dominate the current market[16] and lime spray drying is starting to become significant. Future scrubber technology selections may, in part, be decided upon based on their ability to also control NO_x emissions by simple alteration of the scrubber chemistry. Technologies are currently being developed to take advantage of both the wet and dry scrubber technologies.

Testing of a number of advanced, combined SO_x/NO_x control technologies indicates that performance may be impacted by the SO_x/NO_x ratio and, therefore, the coal sulfur content of the plant being controlled. Table 1-6 shows that there is about an even split between low and medium/high sulfur FGD applications. Since NO_x control performance increases with increasing SO_x/NO_x ratios, higher sulfur market applications become most suitable for such control technologies. Specific technologies in which this parameter appears to be critical are all combined NO_x/SO_x removal processes:

- Wet, FGD scrubber technologies which utilize metal chelates;
- Dry scrubbing technologies which utilize additives such as sodium hydroxide and sodium bisulfite;
- NOXSO process.

Boiler particulate control technology may also be a NO_x control factor based on the ongoing work with spray dryer and duct-injection modification for simultaneous NO_x control. Most of the NO_x reduction has been shown to take place in the filter and, therefore, existing baghouses, plus those planned, could have a significant influence on the selection of NO_x control technology. The dry scrubbing technologies able to remove SO_x and NO_x may also provide greater incentive to invest in baghouse technology. Advanced particulate control technologies may also prove to enhance advanced NO_x control technologies (e.g. the electrostatically augmented fabric filter (EAFF) could enhance dry scrubbing technologies - see Section 6).

The considerable effort going into duct injection technology development as part of the DOE acid rain control program adds considerable significance to the adaptation of this technology for combined NO_x control, if feasible. Since this technology is designed to achieve modest SO_2 removal (50 - 70%), similar NO_x control capabilities would prove to make such a technology extremely valuable. Coupled with a 50% NO_x reduction by combustion modification, a 50% reduction by dry scrubbing would yield an overall NO_x removal of 75%.

By-products can result from NO_x control technologies which will require disposition: sale or disposal. By-product disposal may be complicated by leachable nitrate compounds and nitrogen-sulfur compounds which are characteristic of some of the advanced, combined NO_x/SO_x control technologies mentioned above. Control of such waste product may influence technology selection. On the other hand, by-product sales can

TABLE 1-6

FGD SYSTEMS BY COAL SULFUR CONTENT

Coal sulfur content	Operational		Under construction		Contract awarded		Committed projections		Total	
	No.	MW	No.	MW	No.	MW	No.	MW	No.	MW
Low	68	30,420	7	4,470	7	4,820	13	8,125	95	47,835
Medium	29	11,008	5	2,890	4	2,480	9	5,131	47	21,509
High	38	16,471	3	960	2	1,961	6	3,620	49	23,012
Undecided	-	-	-	-	-	-	15	7,852	15	7,852
TOTAL	135	57,899	15	8,320	13	9,261	43	24,728	206	100,208

result for production of useful commodities such as nitric acid and fertilizers. However, complete NO_x reduction to elemental nitrogen is probably most desirable.

1.7.2 NO_x Control Applications Strategy

As discussed above, the existing boiler market, existing FGD scrubber technology and potentially applicable SO_2 scrubber technology has a strong influence on technology development and selection of NO_x control technology. NO_x control technologies which minimize major hardware additions and/or expensive additive reagents (e.g. low-NO_x burners and additives to FGD systems) have a decided advantage over competing technologies depending on the NO_x reduction requirements.

In order to meet stricter NO_x control requirements, a control strategy must be devised to minimize the total cost impact by utilizing and developing appropriate control technologies. The potential strategies and associated technologies for achieving various levels of NO_x control are identified in Table 1-7.

The use of low-NO_x burners and combustion modifications will almost always be investigated as a primary control; the application of these technologies depends on the site-specific boiler design and operational characteristics. These technologies should be applied initially, if possible, for the following reasons:

- Comparatively low cost compared to other control technologies;
- Minimal to moderate disruption to the boiler and ancillary equipment in many cases;
- Reduction in flue gas emissions typically reduces the capital and O&M cost associated with supplemental flue gas treatment.

Figure 1-7 shows the impact that combustion NO_x control has on subsequent post-combustion control technologies when high NO_x control removal is required; Figure 1-8 graphically represents this control approach and identifies the calculation of the overall NO_x control efficiency. For example, to obtain a total reduction of 80%, a combustion NO_x control of 50% can be combined with a post-combustion control of only 60%. A cost comparison between the combined approach and a flue gas control process designed to achieve the full 80% reduction would very likely show a considerable savings for the combined approach.

The combined NO_x/SO_x control technologies are being developed to serve the existing, uncontrolled boiler market, which is currently even larger than the scrubbed (and to be scrubbed) boiler segment, and a possible new boiler market. Such technologies will be less complicated and more reliable than current scrubber technologies and will also yield useful by-products.

TABLE 1-7

NO_x CONTROL TECHNOLOGY APPLICATION STRATEGIES AND ASSOCIATED TECHNOLOGIES

- Low-NO_x Burners (apply if applicable)
  - Commercially available from boiler suppliers, except for cyclone units

- Combustion modifications
  - Commercially available, if applicable
  - Combine with low-NO_x burners if possible
  - Fuel staging (reburning) may be a possibility when low-NO_x burners & other combustion modifications are not applicable

- Retrofit of existing FGD for combined NO_x/SO_2 removal
  - Wet FGD add-on technologies (e.g. metal chelate processes)
  - Dry scrubber add-on processes (e.g. NaOH additive)

- Combined NO_x/SO_x control technologies for uncontrolled boilers
  - NOXSO process
  - Copper oxide process & other metal oxide-based processes
  - E-Beam Processes
  - Wet FGD with integrated NO_x control
  - Dry FGD with integrated NO_x control

- Flue gas NO_x control - low temperature, after air preheater (less than 300ºF)
  - Low temperature SCR (e.g., activated char & lignite coke)
  - Sodium-based sorbents
  - Gas separation technologies

- Flue gas NO_x control - moderate temperature, after economizer (less than 750ºF)
  - Selective Catalytic Reduction (SCR) processes
  - Solid electrolyte decomposition cells & other electro-catalytic cells (not yet proven at this temperature range)

- Flue gas NO_x control - high temperature, upper furnace (less than 1750ºF)
  - Selective Non-Catalytic Reduction with alternative reducing agents (ammonia, urea, cyanuric acid)
  - Hydrocarbon addition & reburning (usually considered combustion modification)

- Combined combustion and post-combustion NO_x controls
  - See discussion in text

- Combined post-combustion NO_x controls
  - Combined NSCR & SCR
  - Combined gas separation technology with solid electrolyte decomposition of concentrated NO_x stream

FIGURE 1-7

NOx CONTROL COMPONENTS

Combustion vs. Post-Combustion Control

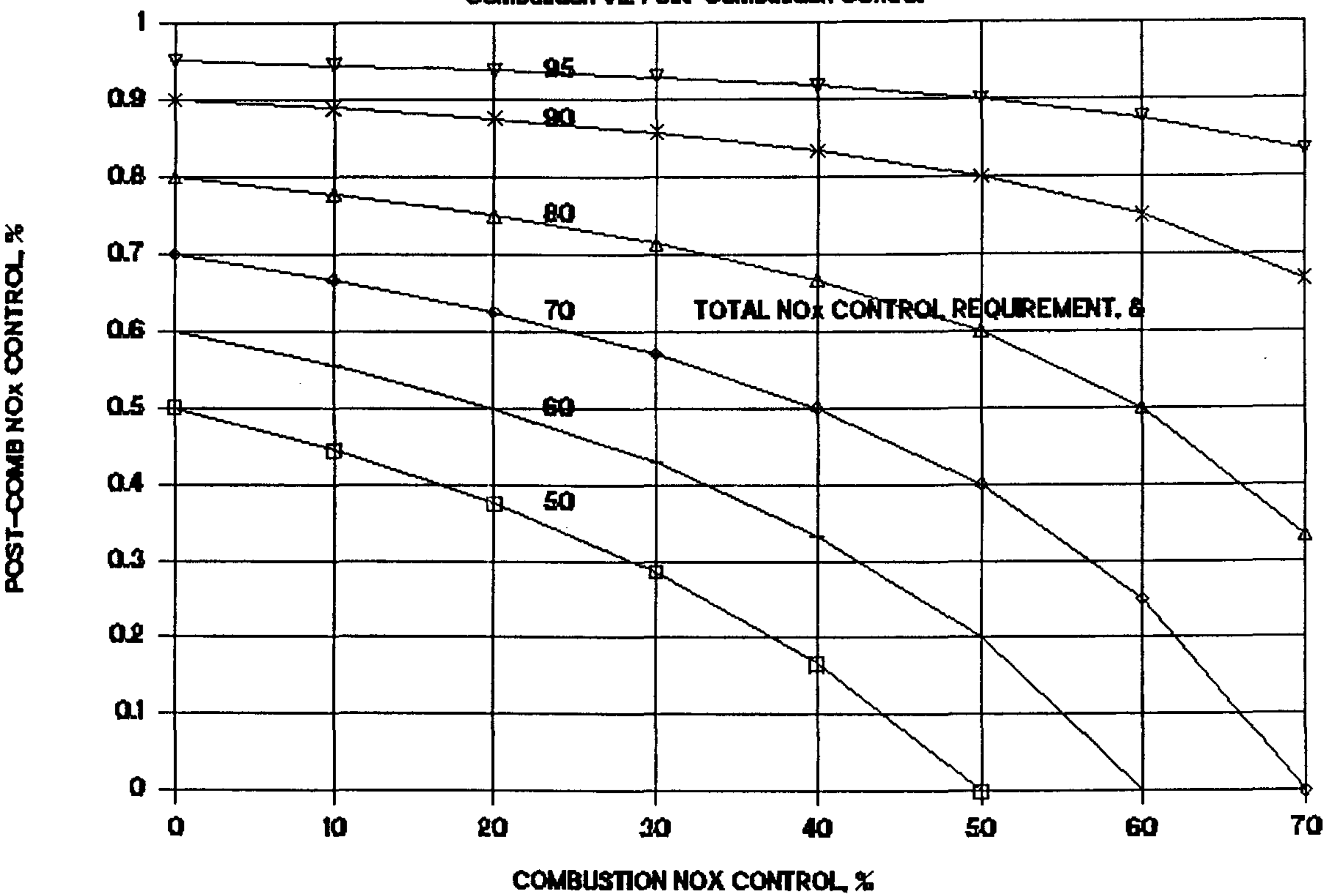
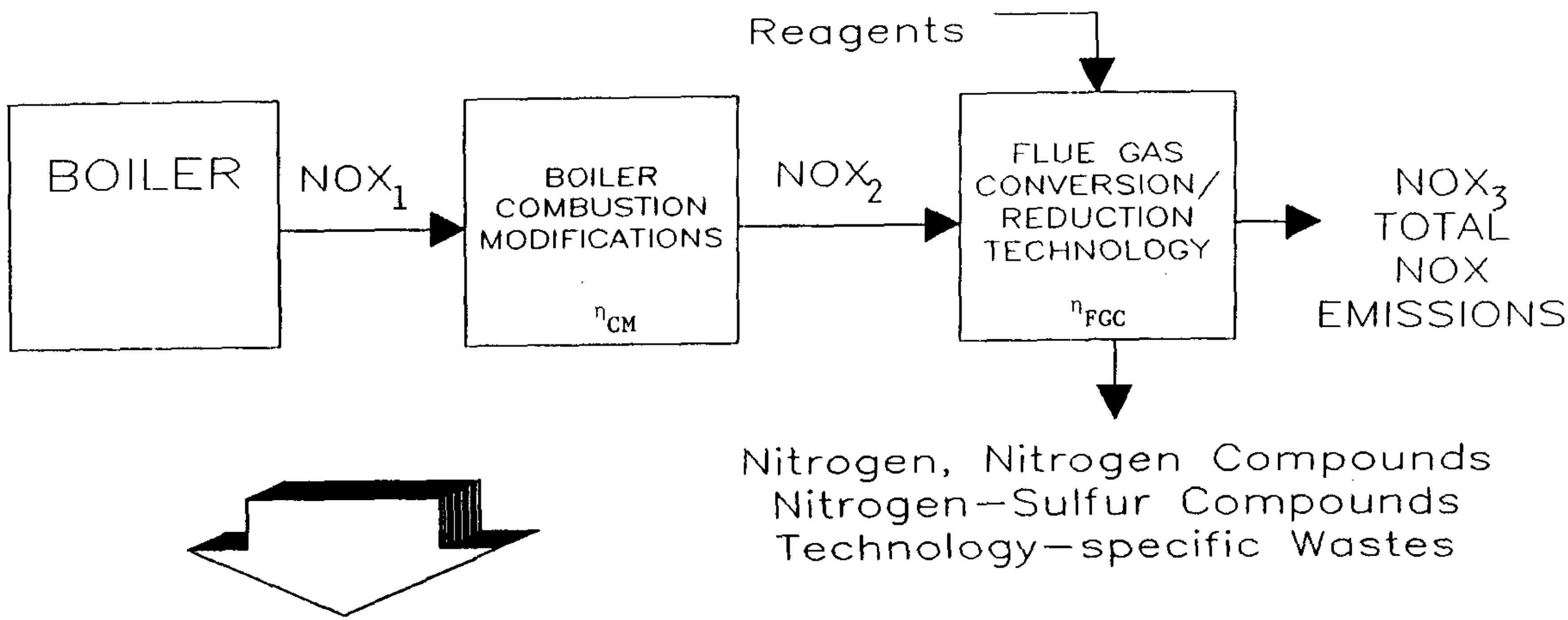


FIGURE 1-8

EXISTING BOILER/NOX CONTROL TECHNOLOGY REPRESENTATION
DIRECT NOX CONVERSION/REDUCTION TECHNOLOGY APPLICATION



TOTAL NOX REDUCTION EFFICIENCY $= 1 - \dfrac{(1-\eta_{FGC})}{1 - (1-\eta_{CM})\,\eta_{FGC}}$

NOX_1 = NO_x originally generated by boiler
NOX_2 = NO_x generated with combustion modification
NOX_3 = NO_x emitted to atmosphere

η_{CM} = Combustion modification NO_x reduction efficiency

η_{FGC} = Flue gas control NO_x reduction efficiency

2. SCR TECHNOLOGY REVIEW AND R&D RECOMMENDATIONS

2.1 SCR Overview

Due to the drawbacks of the wet NO_x control processes, the dry SCR technology has dominated the marketplace due to its greater simplicity and reliability; it is based upon treating the flue gas with ammonia (NH_3) in accordance with the following chemical reactions:

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$

$$6NO + 4NH_3 \longrightarrow 5N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 \longrightarrow 3N_2 + 6H_2O$$

$$6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O$$

These homogeneous gas phase reactions proceed at an acceptable rate when the gas temperature is between 1500°F to 1850°F (800°C to 1000°C), which represents the basis for operation of a <u>selective non-catalytic reduction</u> (SNCR) control method. If hydrogen is introduced with the NH_3, the effectiveness of the reactions can be extended down to 1300°F (700°C). However, in the presence of existing catalyst types, the reactions proceed at a gas temperature ranging between 550°F to 750°F (300°C to 400°C), which is similar to the temperature of the flue gas as it exits the boiler economizer section upstream of the air preheater. This forms the basis for the utility SCR process, which is theoretically capable of achieving 85% to 95% NO_x removal for ammonia injections of 0.85 to 1 mole NH_3 per mole of NO present.

Testing and application of SCR in the United States has been limited due to the less stringent NO_x control regulations in effect and the ability to meet current regulations with combustion modifications and/or low-NO_x burners. Utility-oriented SCR has been tested at two pilot unit demonstrations and one full-scale demonstration. The EPA sponsored a successful 0.5 MW-scale demonstration of the Hitachi-Zosen SCR process at Georgia Power's coal-fired Mitchell Station[1] and a second pilot unit demonstration of SCR was sponsored by the Electric Power Research Institute (EPRI) at Public Service of Colorado's Arapahoe Station[2]. The latter was a 2.5 MW scale application that utilized the Kawasaki Heavy Industries (KHI) SCR technology. The largest SCR demonstration in the United States was recently conducted by Southern California Edison at their Huntington Beach Station[3]. The test utilized the KHI SCR process on a 107.5 MW(e) gas/oil fired boiler and was designed to achieve 90% NO_x removal at loads ranging down to 20 MW(e). Over 18,000 hours of SCR NO_x reduction experience had been obtained at this facility between 1982 and 1985. Table 2-1 summarizes this application. Additional SCR applications in the U.S. are unlikely unless NO_x control regulations are changed. Several detailed engineering economic assessments have also been performed for utility SCR applications. In California, where the state NO_x limitations are more stringent than the

TABLE 2-1

SUMMARY OF SOUTHERN CALIFORNIA EDISON'S SCR $DeNO_x$ SYSTEM (12)

Location	Hunting Beach Unit 2 (gas/oil fuel)
Application Size	107.5 MW
SCR Supplier	Kawasaki Heavy Industries
Test Period	March 1982 - Present
Cumulative Operating Hours	18,000+
NO_x Removal Performance (Design)	90% @ all loads
Ammonia Slip (Design)	10 ppm Max.
Reactor Pressure Drop (Design)	12 in. H_2O
Ammonia Consumption	140,000 lb/year
Energy Consumption	725 kW

Federal regulations, there have been several commercial applications of SCR to industrial boilers, refinery heaters, and stationary engines. California is also requiring SCR on gas turbines used at cogeneration facilities[2]. California's most aggressive NO_x controls are in the South Coast Air Basin, primarily because it is the only region in the U.S. to violate NO_x standards.

2.2 SCR Design Configurations

Flue gas NO_x control systems based on the SCR process can make use of three different equipment design layouts which will significantly impact the location and operation of other power plant components, as well as the design and operation of the SCR reactor. Figure 2-2a shows the "high dust" configuration in which the SCR reactor is located between the plant economizer and air preheater; in this case the catalyst will be subject to the full flue gas dust loading from the boiler. In this configuration the fly ash will be subjected to residual NH_3 contamination and water and solids in the downstream FGD system will also be exposed to NH_3 contamination which may cause disposal/marketing problems. Figure 2-2b shows the "low dust" configuration in which a high temperature electrostatic precipitator (or some other high temperature particulate control device) precedes the SCR reactor in the flue gas stream in order to limit the inevitable catalyst erosion (and possible plugging) caused by fly ash intrusion into the SCR reactor. This configuration prevents fly ash contamination by the NH_3. The third design configuration, which is likely to find its greatest use in retrofit applications with boiler space restrictions, is the "tail end" or "cold side" arrangement shown in Figure 2-2c; while the installation of the SCR process downstream of the FGD process is made considerably more economical for a retrofit application, this advantage must be weighed against an additional expenditure for and operation of a flue gas reheat system. A comparison of these three configurations is made in Table 2-2.

In Japan the high dust system is the preferred equipment configuration based on the following key design premises for coal-fired applications[4,5]:

- o Vertical downward gas flow reactor to prevent ash accumulation;
- o Linear gas velocity of 16 - 20 ft/sec (5 - 6 m/s) at MCR to prevent ash accumulation and erosion;
- o Use of a grid-shaped catalyst with a channel spacing of 0.275 - 0.3 inches (7 - 7.5 mm) to prevent ash accumulation and erosion;
- o Catalyst layers formed without seams along the gas flow direction (possibly with a sacrificial initial stage) to prevent ash accumulation and erosion; and
- o Ash deposition removed by intermittent vacuuming or soot blowing.

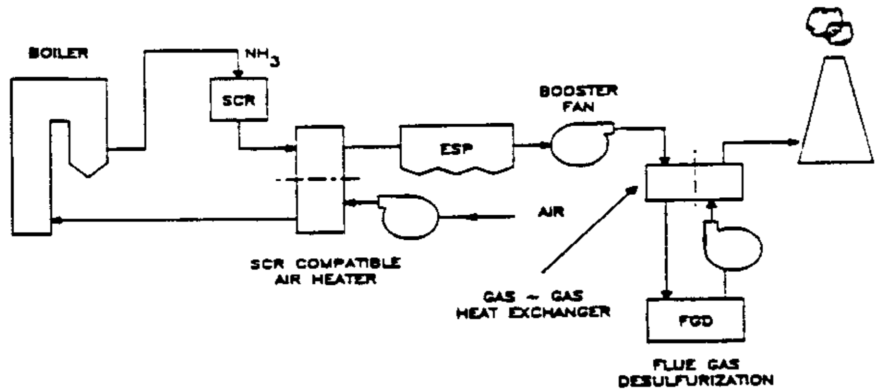


Figure 2-2a. "HIGH ASH" SCR DESIGN CONFIGURATION

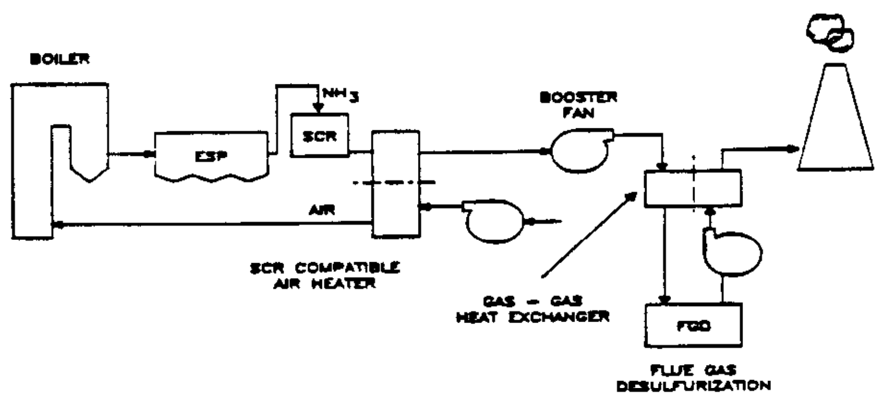


Figure 2-2b. "LOW ASH" SCR DESIGN CONFIGURATION

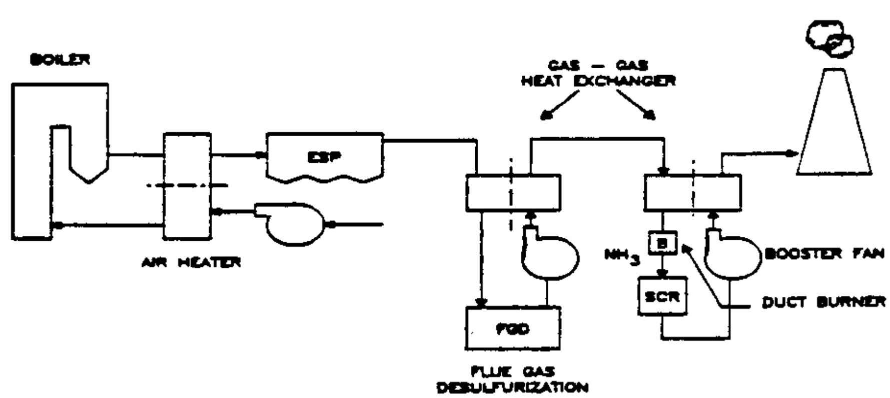


Figure 2-2c. "COLD-SIDE" SCR DESIGN CONFIGURATION

TABLE 2-2

PERFORMANCE COMPARISON BETWEEN SCR DESIGN CONFIGURATIONS FOR COAL-FIRING (6)

Plant Component	High Dust	Low Dust	Cold Side
SCR Reactor			
o Catalyst Life	2-3 years	3-4 years	>4 years
o Plugging by Fly Ash	Prevented by apropriate design and maintenance	Less of a problem-soot blowing still required to remove small ash particles	No problem
o Erosion	Minimized by appropriate design	No problem	No problem
o NH_3 Slip	Reactor overdesign recommended	Same	Same
Air Heater and Gas-Gas Heaters			
o Plugging by Ammonia Salts	Realistically limit NH_3 leakage to less than 5 ppm and SO_3 to less than 2 ppm, appropriate maintenance by soot blowing and water washing	Same	Same
ESP			
o Gas Volume	Base Value	About 1.8 times base value	Base Value
o Physical Size	Base Value	Larger than base value	Base Value
o Fly Ash Removal	Low temperature	Needs ash cooler and insulators	Low temperature
o Fly Ash Treatment for NH_3	Needed	Not needed	Not needed
FGD System			
o Gas-Gas Heat Exchanger	Fine coating of ammonia salts possible-soot blowing required	Soot blowing probably required	No problems
o Waste Water Treatment	Most NH_3 is removed with fly ash-treatment required for off-design performance	Treatment probably required especially for off-design performance	No problems

However, Japan's Electric Power Development Corporation (EPDC) has selected the low dust system based on their comparative tests which indicate that the catalyst lifetime can probably be doubled under low dust operating conditions. Since the catalyst can contribute up to 70% of the system operating costs, dramatic lifetime improvements can substantially impact process economics[4]. Indications are that the German's will not use this particular approach due to their preference for cold ESP's[6].

While not at all typical, both the Japanese and the West German's are making use of the cold-side configuration when boiler and plot-space physical limitations prevent economical installation of the SCR reactor upstream of the preheater. In this case, the FGD outlet gas must be reheated to approximately 600°F (320°C). The largest existing FGD-cold-side SCR system is a 820,000 SCFM (330 MW) 1979 installation at an iron ore sinter furnace of Nippan Kokan KK at its Keihin Works in Japan. It utilizes a rotary regenerative heater followed by ammonia injection and an iron ore catalyst reactor operating at 734°F (390°C) to reduce a 200 ppm flue gas NO_x concentration to 30 ppm. To verify the Japanese experience with the cold-side SCR technology, a 1 MW(e) pilot plant was commissioned in Germany in early 1985 and has been in operation for more than 5000 hours[7]. Very favorable results have been reported: flue gas pressure drop has not increased, the SO_3 content of the flue gas is below 2 ppm, the ammonia leakage is between 5 - 10 ppm and the dust content is less than 0.04 lb/MMBtu (50 mg/Nm^3). Potential corrosion of the catalyst, however, is of major concern.

2.3 SCR System Performance

The performance of a selective catalytic reduction system is based on the following factors:

- NO_x removal efficiency ($NO_{x,out}/NO_{x,in}$);
- Initial NO_x concentration;
- Ammonia consumption required to achieve a specified level of NO_x reduction (NH_3:NO_x stoichiometry);
- Flue gas pressure drop over the catalyst bed (which significantly influences the parasitic energy consumption); and
- Ammonia slip (amount of unreacted ammonia emitted to the atmosphere which is a function of process design and operation and catalyst activity).

The SCR process is typically controlled by the ammonia injection system to maintain a specified NO_x removal ratio and an induced draft fan control system to maintain the proper flue gas flow through the reactor. This requires feed-forward of data from a NO_x analyzer and flow transmitter at the reactor inlet and feedback data from the NO_x analyzer at the reactor outlet.

Japanese SCR manufacturers typically design a DeNOx system for 90% removal with a guarantee of 80% reduction and the system is typically operated between the 65% to 80% removal levels. This reactor over-design is purposefully done in order to avoid significant ammonia leakage to the downstream air preheater and FGD system (configuration 2-2a). Operators typically try to limit the ammonia leakage to 3 - 5 ppm or less to minimize equipment plugging problems with ammonium bisulfate, contamination of fly ash and SO_2 wastewater. Figure 2-3 identifies the conditions under which ammonia salts will form in the air heater and ducts of the power plant. This figure makes it quite clear that both ammonia breakthrough and SO_2 oxidation (to SO_3) must be significantly minimized. Most SCR vendors and users indicate that approximately 0.75 - 1.5% of the inlet SO_2 is oxidized to SO_3 by existing catalysts. Thus, high sulfur coals that produce about 3000 ppm SO_2 could increase the SO_3 concentration by 30 - 45 ppm above the ,roughly, 20 ppm already present; NH_3 concentrations must be extremely low to prevent ammonia salt formation. Additionally, the increased acid dew point, coupled with salt formation, would make it necessary to increase the air heater outlet temperature. Each 10^oF increase in air heater exit temperature can increase the boiler heat rate up to 35 Btu/kWh and significantly increase annual boiler fuel costs.

In contrast to the Japanese operating experience, some German provincial authorities call for close to 90% SCR efficiency in specific applications. One such system is planned for a small installation of VEBA Kraftwerke at Knepper in 1986; the application is for a wet bottom boiler to reduce NO_x emissions to 100 ppm (200 mg/m^3). If conservative design practices are adhered to, the design of the SCR system for 90% NO_x removal could require up to 40% more catalyst than would an 80% removal design[4] which translates into a significant incremental cost.

2.4 Catalyst Activity and Longevity

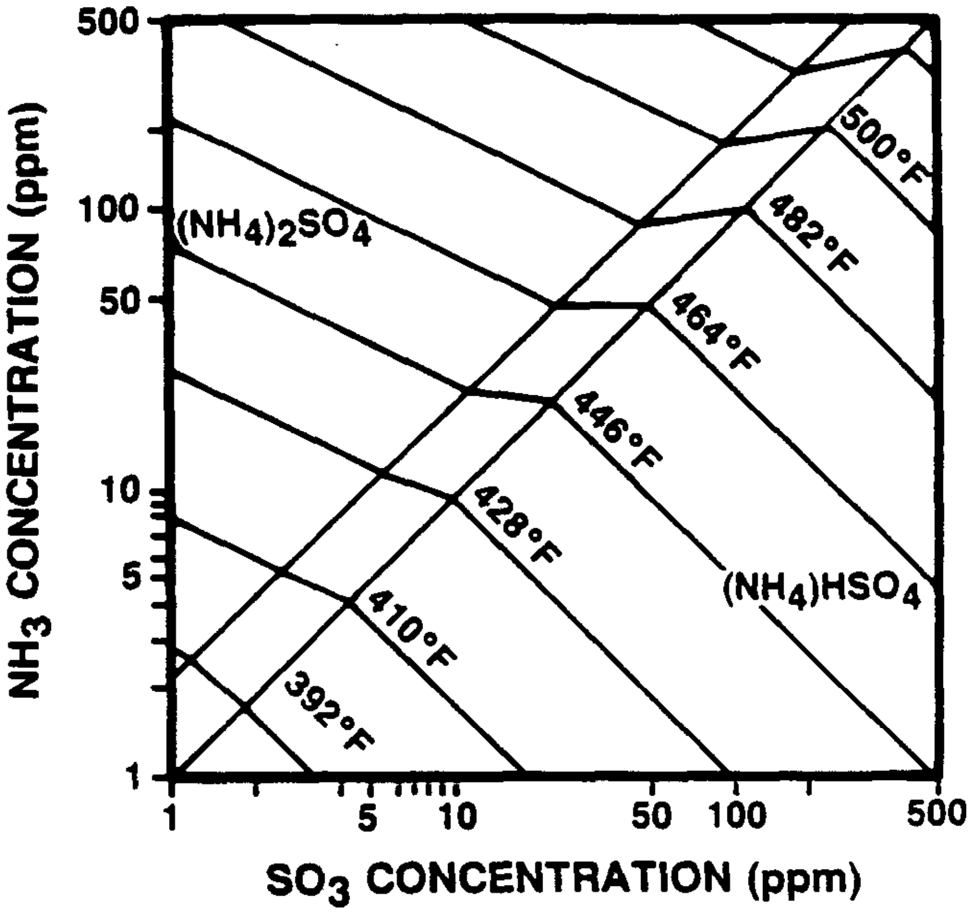
The predominant catalyst type that has been applied in Japan to coal-fired applications, and is now being extensively used in West Germany, is a ceramic-based grid-honeycomb catalyst-type containing TiO_2, V_2O_5 and traces of heavy metals[8]. These catalyst elements are packed into a steel frame to form catalyst modules which are installed into several catalyst layers of the reactor. The typical arrangement for coal-fired applications is shown in Figure 2-4. A key characteristic of a catalyst is the space velocity, defined as:

$$SV\ [h^{-1}] = \frac{\text{flue gas volume flow (wet)}}{\text{volume of catalyst}} \qquad \frac{ft^3/h}{ft^3}$$

The catalyst space velocity (and catalyst cost) are determined by NO_x removal requirement, initial NO_x concentration, and permissible residual

FIGURE 2-3

CONDITIONS FOR THE FORMATION OF AMMONIUM SULFATE/BISULFATE



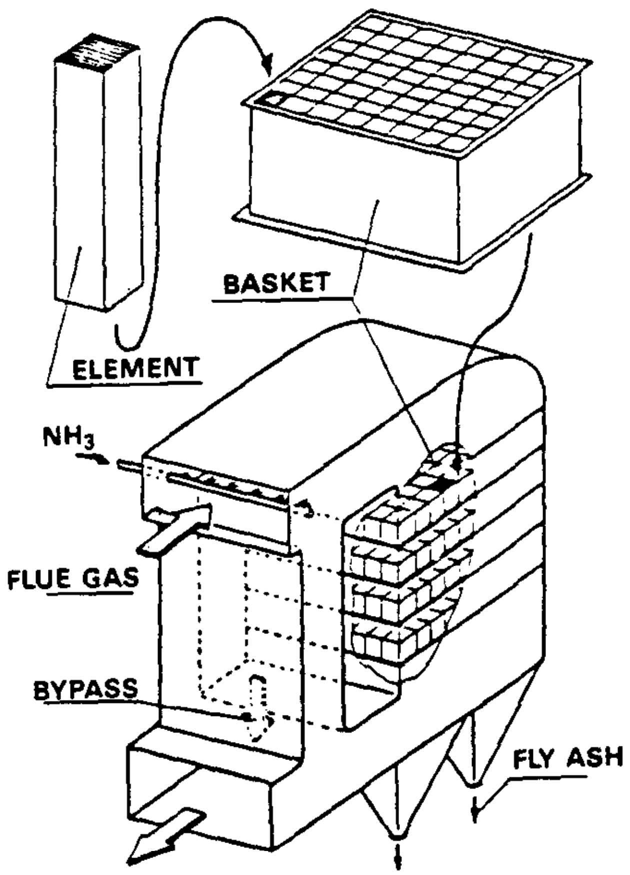


FIGURE 2-4. GENERAL ARRANGEMENT OF SCR CATALYST (16)

NH_3. Typical SV values for catalysts applied to coal-fired plants range between 2500 - 3000 h^{-1}. Current design practice in Germany uses a space velocity of 2500 h^{-1} for slag tap furnaces with high NO_x concentrations in the flue gas and a value of 3500 h^{-1} for dry bottom furnaces with lower NO_x generation. Thus, for a 100 MW plant, this results in an approximate catalyst demand of 5000 ft^3 (130 m^3) for the slag tap furnace and 3200 ft^3 for a dry bottom furnace[8].

Figures 2-5 and 2-6 summarize the catalyst space velocity and geometry for seven full-scale SCR systems currently operating in Germany; Figure 2-5 indicates the relationship between space velocity and design NO_x removal efficiency, and Figure 2-6 shows the relationship between space velocity and initial NO_x concentration[11]. All of these plants have reported achieving the 120 ppm (@ 3% O_2) regulation with residual NH_3 of less than 2 ppm. Note that catalyst space velocity appears to decrease linearly with the required NO_x removal efficiency. Figure 2-6 indicates a somewhat linear relationship between space velocity and initial NO_x concentration up to about 500 ppm, with additional NO_x concentration increases having a diminished impact.

High dust applications of existing SCR technology in the U.S. on high sulfur coals may be difficult to execute because of the need to limit space velocities to achieve very low residual NH_3; low space velocities increase SO_2 to SO_3 oxidation. Thus, simultaneously achieving low residual NH_3, low SO_3 concentrations, and meeting high NO_x removal requirements may not be possible for high sulfur U.S. coals. Low fly ash alkalinity also exacerbates the problem due to limited SO_3 reduction.

The current SCR R&D emphasis in Japan is on increasing catalyst activity so as to minimize the catalyst requirement and the amount of unreacted ammonia escaping from the catalyst. It is now common for the slip ammonia to be below 5 ppm due to new, more reactive catalysts and partly by specifying a low space velocity[9]. Catalyst development is a compromise between NO_x removal activity and SO_2 to SO_3 conversion ratio; minimizing SO_2 oxidation and ammonia slip is the key to preventing ammonium bisulfate formation in downstream equipment.

Three of the principal catalyst deactivation mechanisms are surface masking, poisoning of active catalyst sites by sulfate compounds and other trace fuel species and erosion by abrasive fly ash. Surface masking appears to be increased by fuel characteristics that promote high SO_2 and SO_3 concentrations. These fuel characteristics are:

- o High levels of fuel sulfur;
- o High fly ash iron content (which helps catalyze SO_2 to SO_3 in the boiler); and
- o Low ash alkalinity (absorbs or buffers SO_3).

Poisoning by trace metals, such as potassium, has also been identified as a possible catalyst deactivator. High ash silica content produces more

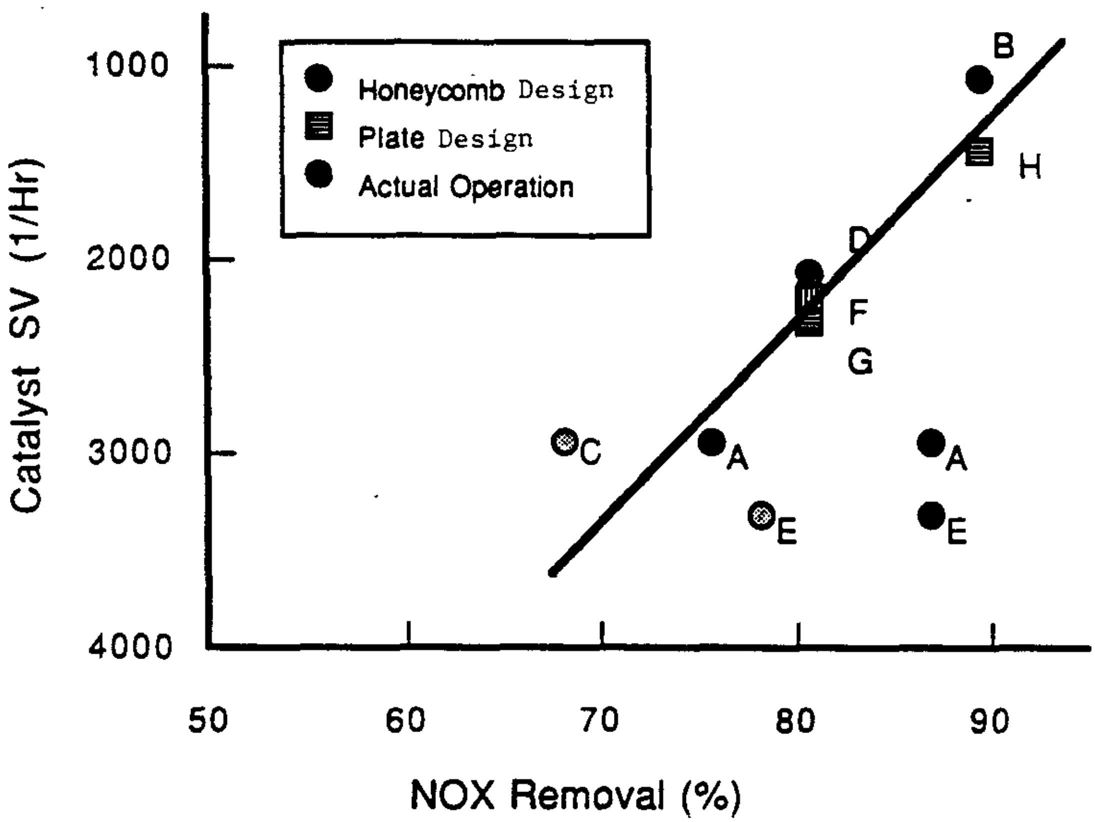


FIGURE 2-5 **CATALYST SPACE VELOCITY Vs. NOx REMOVAL EFFICIENCY**

Source: EPRI

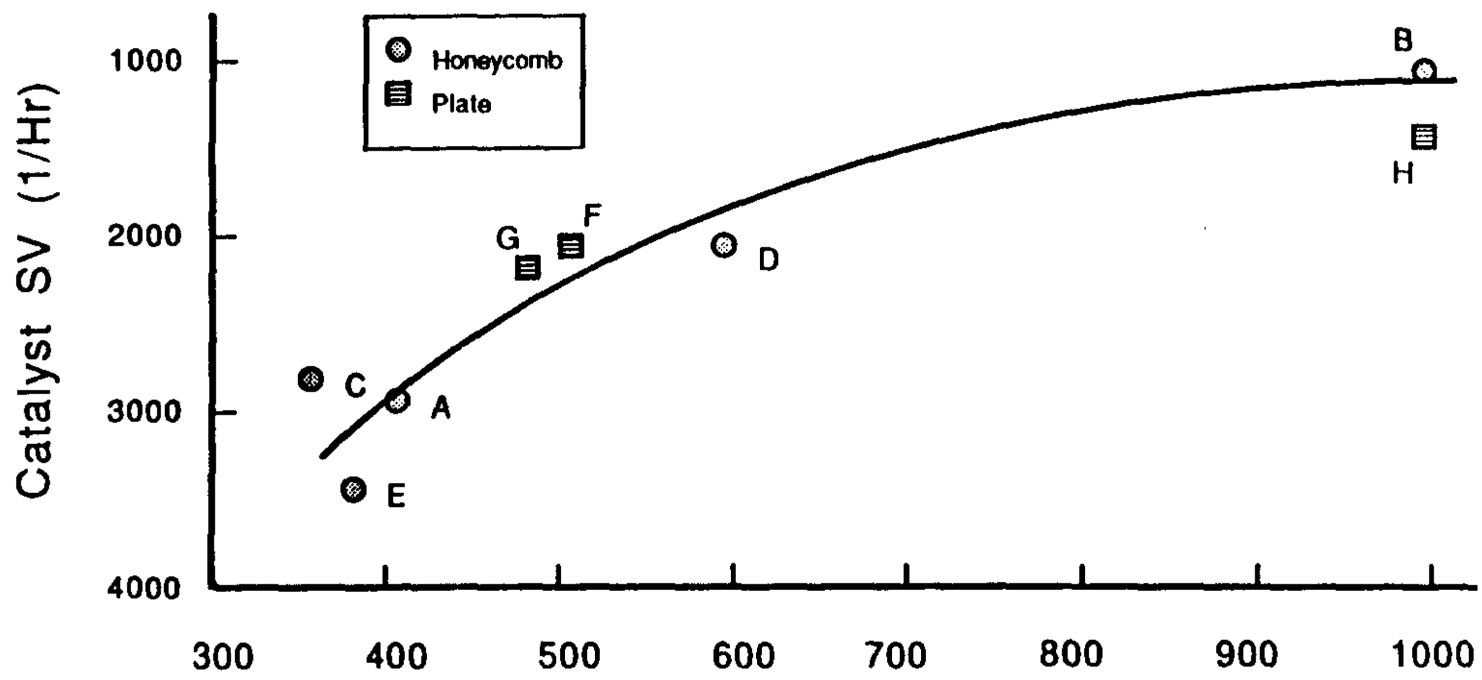


FIGURE 2-6. **CATALYST SPACE VELOCITY Vs. INITIAL NOx CONCENTRATION** - DESIGN CONDITIONS

abrasive fly ash which can erode the catalyst in high dust applications. More meaningful data are being accumulated on catalyst longevity in Japan based on early 1980 installations on coal-fired facilities. Two-year catalyst guarantees have become common in the industry. Currently, some of the installations have catalyst that has been in operation for four to five years. It is expected that the "low-dust" and "cold-end" SCR configurations will yield catalyst lifetimes of at least 4 to 5 years due, in part, to a cleaner catalyst operating environment and because the control of ammonia leakage (below 5 ppm) loses its importance since possible deposits of ammonia products in the air heater, as well as problems associated with fly ash and waste water contamination don't arise.

The difficulty in determining the true life of the full catalyst load is that the entire charge is seldom replaced at one time. As discussed previously, the usual Japanese practice is to install the catalyst in layers; when the overall efficiency drops, one or more layers are replaced to return the unit to its required performance level. Unless careful records are maintained (and made available), it is difficult to concisely establish the "life" of the catalyst[9]. In addition, it is important to account for the actual hours of catalyst operation when considering the calculation of a catalyst lifetime.

2.5 Recent Operating Experience & Lessons Learned in Japan and Germany

Recent operating experience with SCR systems shows continued operational problems in three major areas:

- Plugging of the air heater and other downstream equipment with ammonium bisulfate and ammonium sulfate;
- Ammonia bypass leakage with a resulting contamination of the fly ash and FGD wastewater; and
- Maintenance and accuracy of the NO_x and NH_3 control instrumentation.

Current operations in Japan and Germany indicate that fouling of equipment downstream of the SCR reactor can be expected when NH_3 concentrations in the treated flue gas are as high as 5 ppm, especially when the SO_3 concentration exceeds 2 ppm. Such conditions are typically encountered when the SCR process is operated at NO_x removal efficiencies higher than 80% or, even at lower efficiencies, when nearing the end of the usable lifetime of the catalyst (when NH_3 feed increases to maintain NO_x removal efficiency). The recent SCR tests at Southern California Edison's Huntington Beach Station, which was designed for 90% NO_x removal, showed heavy deposits of ammonium bisulfate and iron sulfate in the intermediate zone of the air heater, while the inlet (hot) and outlet (cold) zones were not affected. After about 1400 hours of operation, the deposits increased the pressure drop across the air heater by about 50%[3]. In reducing the flue gas temperatures to as low as 300°F to 450°F (150 - 230°C) the air heater causes the excess ammonia vapor from the SCR operation to react with water vapor and most of the SO_3 present to form the ammonium bisulfate and ammonium sulfate. The SCR reactor can compound the problem since the catalyst typically converts about 1% of the SO_2 to SO_3, although new catalyst designs by Japan's IHI claim conversions of less than 0.5% for 90% NO_x removal levels[5]. Ammonium sulfate vapor solidifies below 480°F (250°C) and ammonium bisulfate forms a liquid at a slightly lower temperature and solidifies at approximately 300°F (150°C). Experience has shown that the air heater, when so wetted and fouled, acts like "fly paper" in scavenging fly ash particles from the flue gas, further contributing to internal deposits causing increased gas pressure drop. Based on prior field evaluations in Japan and more recent tests in Germany[10], the following key criteria have been established for the design of SCR-compatible air heaters (and gas-gas heaters for cold-side SCR):

- The heat transfer surfaces must be configured such that they are easily cleaned by means of high efficiency soot blowing;
- The cross-over of heating surface layers must be avoided in the areas most likely to be affected by ammonium bisulfate deposition;
- Enameled heating surfaces should be used, particularly when the SO_3 concentration is expected to be greater than 2 ppm;
- When SO_3 concentration is greater than 2 ppm provisions should be made for frequent off-line water washing, unless in-service "isolated" washing can be performed. Japan's Chugoku Electric recently developed a method of thermal cleaning that they believe is superior to water washing[4].

A major operational problem is the accurate measurement of ammonia and NO_x in the flue gas and the maintenance of the associated monitoring equipment. The principal causes of these problems appear to be a result of: the low gas concentration levels to be measured by the instruments; the presence of other contaminants which interfere with the measurement; the large duct geometry which can lead to sampling errors; and the plugging of sampling lines with condensed ammonia products[4]. The recent SCR tests at Southern California Edison's Huntington Beach Station experienced frequent plugging of sampling lines and chemiluminescence-type NO_x monitors; it was eventually found necessary to heat trace the sample lines to about 600°F (316°C) and use one-half inch stainless steel tubing to minimize pluggage. A more conservative (and expensive) solution to the problem is to overdesign the catalyst reactor and operate at conservative removal levels to assure that NH_3 leakage levels and NO_x levels remain at such low levels that it isn't important to know their exact absolute values. The Takehara plant, in Japan, simply cuts off the ammonia supply as load is reduced on it's Unit #1 SCR system. Promising results for continuous ammonia-slip measurement have been obtained in Japan by using ultraviolet absorption. European SCR experience will definitely assist determining 1)specifications for flue gas flow rate, temperature and composition monitors, 2) flue gas NH_3 monitors, 3) maintenance procedures and 4) equipment sparing philosophy.

Experience in Europe should be a good indicator of catalyst lifetime for most low-sulfur U.S. applications of SCR with existing catalysts. However, the different trace element compositions of U.S. coals should be accounted for in catalyst design. It is unlikely that the German SCR experience will provide enough information to proceed with high sulfur coal applications. Representative pilot-scale R&D will be required.

2.6 Process Integration and Retrofit Factors

The general practice in Japan is to precede the SCR with a high degree of combustion modification, since the latter is the less expensive of the two technologies[9]. By use of low-NO_x burners plus overfire air and reburning (staged combustion) the NO_x concentration can be reduced by 50 - 70% for most coals. If an SCR system is still required to achieve greater emissions reduction, the catalyst size and ammonia consumption will have been substantially reduced.

The selected process configuration will impact other plant components and plant operation. In the "high dust" configuration operational experience indicates that most of the ammonia leakage past the reactor is removed by the ESP and codeposited with the fly ash. Depending on the particular NH_3 concentration in the ash, disposal or sale may be affected as a result of the ammonia odor. Similarly, if a wet FGD process is downstream of the SCR system, ammonia may also find its way into the waste water of that process; further waste water processing may be required.

The three major problems associated with retrofit of the SCR technology to existing plants are 1)lack of space between the economizer and air heater for the SCR equipment, 2)low flue gas temperatures exiting the economizer (at MCR and reduced loads) and 3)existing fans are unable to handle the additional pressure drop associated with the SCR reactor and new ducts. Air heaters are usually located very close to the steam generator economizer, which requires it to be moved or, if possible, ductwork can be installed around it, which can make for very complicated inlet and outlet configurations. A schematic of an MHI system shown in Figure 2-7 demonstrates the potential for ductwork complexity when retrofitting the SCR process[11]. The low flue gas temperature problem is usually handled by reducing economizer heating surface or installing economizer bypass ducts and dampers (as shown in Figure 2-7). Installation of additional booster fans is required to deal with the added gas pressure drop of the SCR reactor.

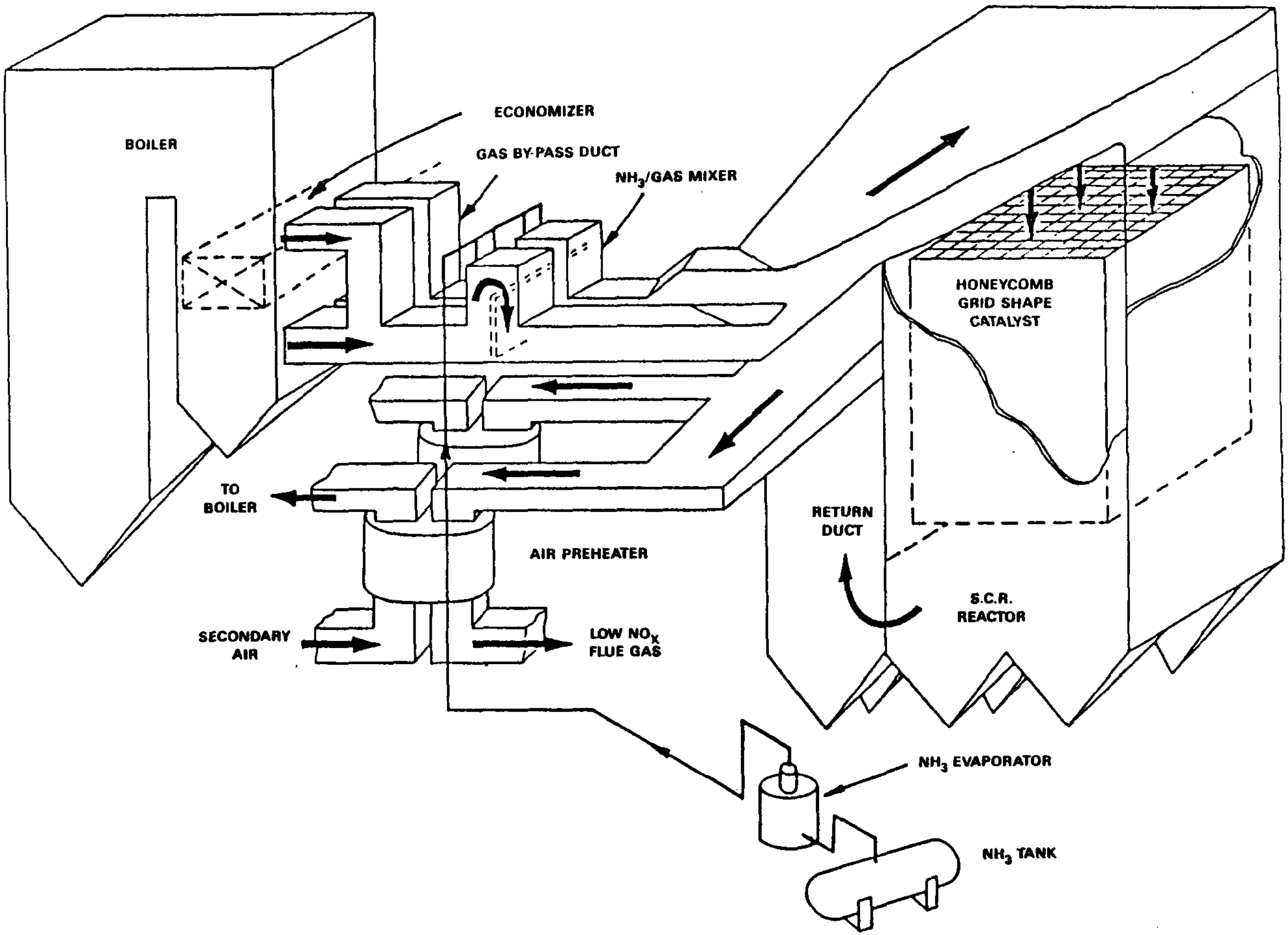


FIGURE 2-7. **POSSIBLE SCR SYSTEM DUCTWORK LAYOUT (2)**

2.7 Catalyst Data

The ideal SCR catalyst should have the following characteristics:

- o Highly active over a wide temperature range (high space velocity);
- o No poisoning by SO_x;
- o Long lifetime;
- o Require a minimum amount of reducing agent;
- o Low cost.

Over the past decade thousands of catalyst compositions have been tested and patented, especially in the U.S. and Japan. Tables 2-3 to 2-8 categorize many of the catalysts tested and currently being used[12]. These tables list probable operating temperature ranges, approximate space velocity for specified emission reduction, the approximate NOx/SO_x concentrations used in tests and the NH_3/NO_x ratios observed to achieve the listed emissions reduction. The potential low-temperature catalysts are marked. The key categories are:

- o Noble metals, such as Pt-Rh, Pt-Pd supported on Al_2O_3 or SiO2-Al_2O_3;

- Used for decoloration (reduction of NO_2 to NO)
- Operate at low efficiencies
- Low temperature operation yields SO_2 poisoning
- High temperature operation causes loss of activity due to chemisorption of oxygen
- Require high NH_3/NO_x ratios (1.6 - 2.5)

- o CuO and Cu salts supported on Al_2O_3 (Table 2-3);

CuO-based catalysts:

- Potential for combined NO_x/SO_x removal since $CuSO_4$ acts as the reduction catalyst
- Relatively high operating temperatures required (700 -800°F)
- Space velocities for existing processes are somewhat low (3500-7000 hr^{-1})
- Low NH_3/NO_x ratios required for high efficiency reduction

Cu salts:

- Potential for very low catalysis temperatures
- Space velocities unknown

- o Copper-containing catalysts on different supports (Table 2-3);
  - Mixed metal oxides (e.g., Cu, Mn, Ni oxides on Al_2O_3) have potential for relatively low operating temperatures and high space velocities but NH_3/NO_x ratios can be very high

- o Fe_2O_3 and Fe_2O_3 mixtures unsupported or supported on Al_2O_3 or SiO_2-Al_2O_3 (Table 2-4);
  - Require high operating temperatures
  - Operate at relatively low space velocities
  - Potential for low cost

- o V_2O_5-containing catalysts (Table 2-5);
  - High activity @ relatively low temperatures
  - V_2O_5 reduces sulfur poisoning, but may catalyze SO_2 oxidation to SO_3
  - V_2O_5-WO_3 has potential as low temperature catalyst, but could be expensive

- o CeO_2-containing catalyst (Table 2-6);
  - Very high space velocities possible
  - High operating temperatures
  - Should be evaluated in combination with other metal oxides

- o Base metal oxide supported on TiO_2 (Table 2-7);
  - TiO_2 offers greater resistance to SO_2 poisoning
  - Potential for high space velocities
  - Basis for many existing commercial catalysts

- o Base metal on activated carbon and lignite coke; and
  - Potential for lower-temperature operation
  - Also captures SO_2
  - Low space velocities
  - High carbon oxidation and attrition

- o Zeolites (Table 2-8).
  - Potential for lower temperature operation
  - Relatively high space velocities.

2.8 SCR Economics

The inconsistent methods used to calculate the capital and operating costs for SCR plants by various organizations and analysts in different countries (without adequate documentation of their evaluations) makes it difficult to

TABLE 2-3

CATALYSTS CONTAINING COPPER/COPPER OXIDES

Composition	Temp °C	Space Velocity h^{-1}	SO_x/NO_x concn, ppm v/v NO_x	SO_2	NH_3/NO_x	Reduction %
CuO/Al_2O_3	250-400	3500-7000	500	3000	1.1	90
Cu-pyrophosphate/Al_2O_3	400	14000	126	520	1.1	91.4
$CuCl_2$-V_2O_5-Al_2O_3	<120	--	300	200	--	90.0
Cu, Ni, Mn oxides/Al_2O_3	180-250	12000	1000	--	4.7	90.0
CuO-TiO_2-V_2O_5	325	10000	200	800	1.0	99.0
Cu, Mn, Fe oxides/Al_2O_3	350	5000	--	--	--	80-90
Cu, Cr, Co, Ni, Zn, Mn/Si_3N_4, $FeSO_4$	250-400	5000	300	350	1.0	90-95
Cu, Cr, Co, No, Zn, Mn/spinel type ferrite	400	5000	300	--	0.8	97.0
Fe, Cu/Al_2O_3-SiO_2	260-380	10000	100-150	0-500	1.0-1.5	80-98

TABLE 2-4

CATALYSTS CONTAINING IRON COMPOUNDS

Composition	Temp °C	Space Velocity h^{-1}	SO_x/NO_x concn. ppm v/v NO_x	SO_2	NH_3/NO_x	Reduction %
$Fe_2(SO_4)_3$	270-400	--	400	300	1.2	56-99
Fe_2O_3-Cr_2O_3-$Al_2(SO_4)_3$	200	--	1000	--	1.1	90.5
Fe_2O_3 from spent pickling liquor	340	4000	200	50	1.3	90.0
Fe sphere/fluidized bed	--	--	200-300	300-2000	1-1.5	75-78
iron sand	400	5000	500	2000	1.5	50.0
dust from mineral sintering furnace (Fe and FeO)	300-350	2000	250	--	2.0	80.0
converter slag containing Fe and Mn oxides	300-350	1000	250	--	2.0	90.0
Fe_2O_3/SiO_2-Al_2O_3	--	--	200	1000	1.1	90.0
ore slag	310	500	200	500	2.5	90.0
Fe_2O_3-Cr_2O_3/SiO_2-Al_2O_3	250-350	--	200	1000	1.35	90-97.5
Fe + W oxides/SiO_2-Al_2O_3	350-450	--	--	--	--	90-95
Fe_2O_3/SiO_2-Al_2O_3	380	--	--	--	--	90.0
Fe_2O_3-vanadium sulfate/SiO_2-Al_2O_3	330	3000	760	1050	1.3	88.0

TABLE 2-5

CATALYSTS CONTAINING VANADIUM OXIDES

Composition	Temp °C	Space Velocity h^{-1}	SO_x/NO_x concn. ppm v/v NO_x	SO_2	NH_3/NO_x	Reduction %
$V_2O_5/Fe_2O_5/Al_2O_3$	350	5000	150	150	1.0	90.0
V_2O_5/Al_2O_3	300	10000	120	--	1.0	80.0
V_2O_5 or base metal	330-370	--	115	--	--	99.8
V_2O_5, WO_3/Al_2O_3	180-300	10000	500	250	1.0	60-100
$VOSO_4$, $SnCl_4/SiO_2$	350	4000	750	850	1.3	91.0
V_2O_5, SnO_2/SiO_2	300-450	10000	750	800	1.3	79-89
V, Nb, Ti and Cu oxides/Al_2O_3	300	--	--	--	--	97.2
V_2O_5/Al_2O_3	250-350	13500	231-1251	--	1-4.0	77-98

TABLE 2-6

CERIUM CONTAINING CATALYSTS

Composition	Temp °C	Space Velocity h^{-1}	SO_x/NO_x concn, ppm v/v		NH_3/NO_x	Reduction %
			NO_x	SO_2		
CeO_2/Al_2O_3	480-500	40000	2000	--	1.0	94.0
CeO_2, V_2O_5/Al_2O_3	450	--	3000	--	--	--

TABLE 2-7

CATALYSTS CONTAINING BASE METAL OXIDE(S) ON A TITANIUM OXIDE SUPPORT

Composition	Temp °C	Space Velocity h^{-1}	SO_x/NO_x concn, ppm v/v		NH_3/NO_x	Reduction %
			NO_x	SO_2		
TiO_2-CeO_2 (10-20 mesh)	400	50000	300	--	1.1	90.0
TiO_2-CeO_2-MoO_3	200-400	50000	300	--	1.2	98.0
TiO_2-V_2O_5/inert support	300	10000	200	--	1.35	99.5
TiO_2-MnO_2	450	5000	300	800	1.33	86-90
TiO_2-WO_3-V_2O_5-BiO_3	250	10000	200-230	3000	1.0-1.1	82.0
TiO_2-CuO	330	10000	300	800	1.0	90.0
TiO_2-V_2O_5	323	10000	200	800	1.0	99.0
TiO_2-V_2O_5	380	--	--	--	--	89.0
V_2O_5/TiO_2 ceramics	300	10000	--	--	--	99.0
TiO_2-SiO_2-ZrO_2	300-400	20000	200	800	1.0	93-96
V, Mo, W, Cu, Cr/TiO_2	200-500	10000-500000	100-210	--	0.5-10	50-99

TABLE 2-8

ZEOLITIC CATALYSTS

Composition	Temp °C	Space Velocity h^{-1}	SO_x/NO_x concn, ppm v/v NO_x	SO_2	NH_3/NO_x	Reduction %
natural zeolite + Fe ore	250	5000	190	--	1.0	70.0
natural zeolite + Cu	200-300	--	190	--	1.05	95.0
zeolite + Fe_2O_3	300	5000	190	--	1.1	98.0
zeolite + Cu	200	5000	250	--	1.0	--
natural zeolite + V_2O_5 + Fe_2O_5	360-390	3600	110-150	4000	1.5-2.0	--
H-type zeolite + CuO	350	20000	250	3000	1.0	98.0
synthetic mordenite	200-300	15000	6520	--	0.8	--
natural or synthetic zeolite and alkali earth metal	300-450	5000-30000	100-500	100-500	--	80-85

present definitive SCR costs and cost comparisons. The intent of the cost data described here is to provide some perspective on the magnitude of expected SCR costs and their relative sensitivity to key plant elements.

The Tennessee Valley Authority (TVA) recently completed a utility emissions control cost study for the U.S. Environmental Protection Agency (EPA) which included selective catalytic reduction for NO_x control[13]. The results are presented in Table 2-9 along with information pertinent to the specific cases evaluated. Table 2-10 provides a breakdown of the equipment cost areas for the TVA case 1 (500 MW, 80% NO_x removal). It is very important to note that the initial catalyst charge accounts for almost one-third of the total capital investment for the process. Most of the remaining capital costs are for the reactor and associated internal and external catalyst supports and handling system, and for the flue gas handling system (ductwork and booster fans - 90% of the flue gas handling system costs is for the ductwork). According to this study, the ammonia storage and injection system, air heater modifications and waste disposal (of spent catalyst) only represented about 5% of the total capital investment. Total capital investment for NO_x control in case 1 is lowest for all plant sizes because most of the capital costs are directly related to flue gas volume which is inversely proportional to the heating value of the coal. The case 3 capital cost is projected to be lower than case 2 because of the cleaner flue gas coming from the hot ESP.

Table 2-11 provides the associated breakdown of the operating costs for the TVA case 1 application. The catalyst replacement cost dominates the operating costs: over 80% for a two year replacement schedule. Increased catalyst longevity and better performance (high space velocities) can, therefore, substantially reduce these costs. Due to the high annual charge for catalyst replacement, the operating cost is relatively insensitive to the cost of ammonia.

The relative cost differential between the "high ash" and "cold-side" SCR design configurations has been explored by West German economic evaluations[6]. Figure 2-8 compares the relative capital investment requirements for these two configurations which indicates an approximate 40% cost advantage for the hot-side approach. However, for a difficult SCR retrofit application, the cost difference between the two configurations could be substantially reduced. Figure 2-9 compares the total annualized cost of the two configurations for two different plant sizes and applications as a function of annual operating time. The substantial difference in cost between the two configurations reflects the capital cost difference and the added reheat costs required by the cold-side design. However, this particular study did not give any credit to the cold-side SCR system for reheat after an FGD process; when an appropriate credit for reheat is given, the margin of cost difference between the hot and cold-side design is further reduced.

Cold-side installations in West Germany to date are all small capacity with poor economies of scale[14]. A municipal power plant, which is installing three 35 MW(e) cold-side SCR systems utilizing a cyclical operation of twin granular heat-exchange beds in conjunction with feed ammonia to a single catalyst chamber operating at 662°F (350°C) to reduce NO_x emissions to 200

TABLE 2-9

RECENT U.S. SCR COST ESTIMATES

($1986, TWO-YEAR CATALYST LIFE)

	PLANT SIZE, MW (e)			
	200	500	500	1000
NO_x Removal, %	80	80	90	80
Capital Cost, $/KW				
Case 1	106	86	99	80
Case 2	125	103	114	98
Case 3	125	99	111	94
First Year Operating Cost, Mills/KWH				
Case 1	3.2	3.2	4.0	3.2
Case 2	3.9	3.9	4.5	3.9
Case 3	3.7	3.7	4.2	3.7

MAJOR DESIGN CONDITIONS

	CASE 1	CASE 2	CASE 3
Coal	EAST BIT.	WEST SUBBIT.	WEST SUBBIT.
Btu/lb, as fired	11,700	8,200	8,200
NO_x emitted lb/10^6 Btu	0.6	0.5	0.5
Plant Heat Rate, Btu/KWH	9,500	10,500	10,500
SCR Configuration	High Dust	High Dust	Low Dust
Includes Air Heater Modifications	Yes	Yes	Yes
Economizer Bypass for Temp. Ctl	Yes	Yes	Yes

TABLE 2-10

EQUIPMENT COST BREAKDOWN FOR TVA BASE SCR APPLICATION (18)
(500 MW 80% NO_x REMOVAL, $1986)

EQUIPMENT AREA	**$/KW**	**TOTAL % OF PROCESS CAPITOL**
NH_3 Storage Injection	2.71	5.1
Reactor	15.13	30.3
Catalyst	24.78	46.5
Flue Gas Handling	7.92	14.9
Air Heater Modification	1.69	3.2
TOTAL PROCESS CAPITAL	53.23	100.0
Waste Disposal	0.04	0.08
Land	0.02	0.04
Royalty	0.95	1.8
Other[1]	32.00	60.1
TOTAL CAPITAL INVESTMENT	86.24	162.0

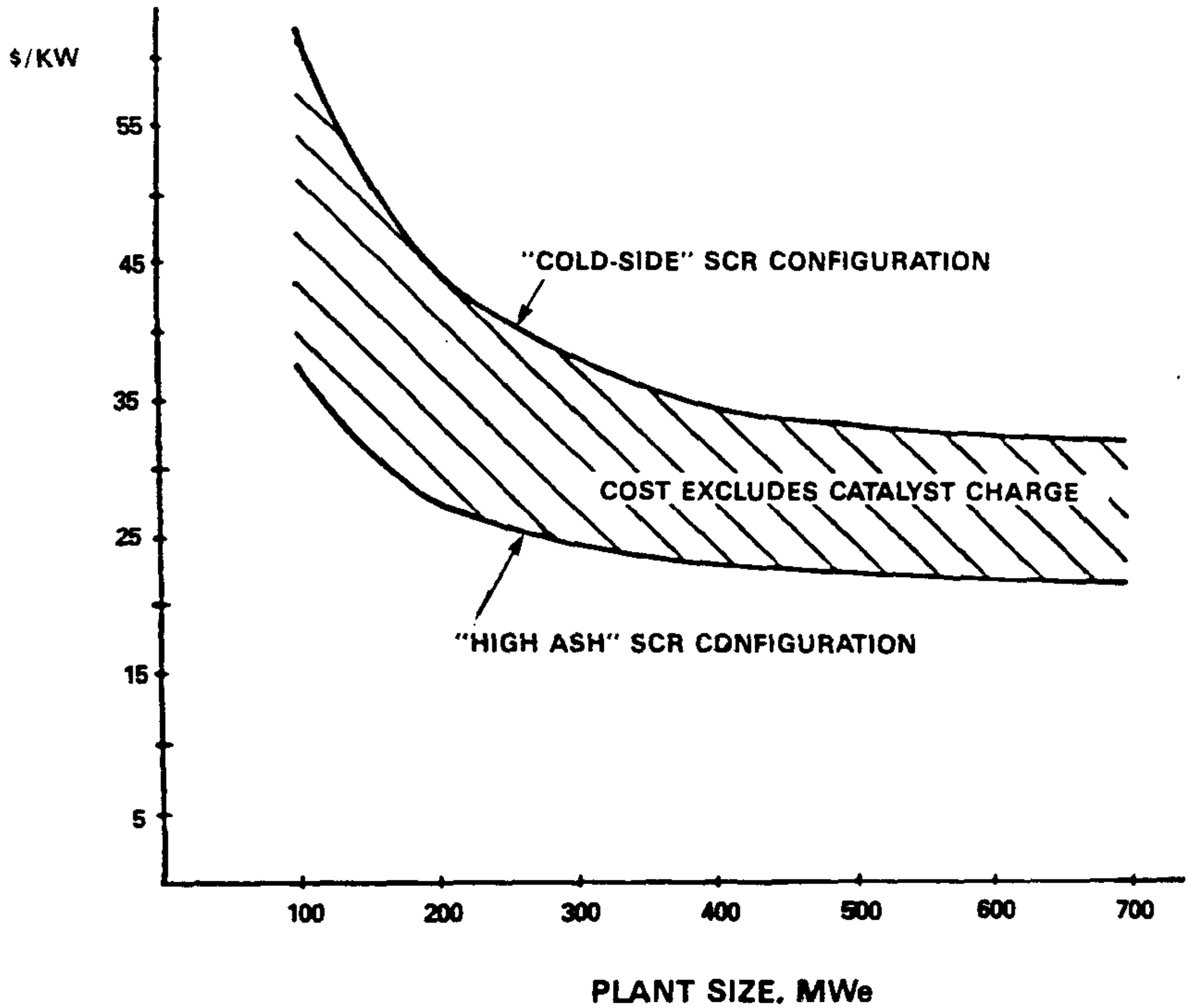
NOTE:

1. Consists of indirect capital investment, allowance for startup and modifications, interest during construction, working capital, services, utilities and miscellaneous.

TABLE 2-11

OPERATING COST BREAKDOWN FOR TVA SCR APPLICATION (18)
(500 MW, 80% NO_x REMOVAL, 2-YEAR CATALYST LIFE, $1986)

DIRECT COSTS	**MILLS/KWH**	**ANNUAL % OF REVENUE REQUIREMENT**
Ammonia	0.13	4.1
Catalyst	2.53	79.3
Operating Labor and Supervision	0.03	0.9
Steam	0.02	0.6
Electricity	0.10	3.1
Fuel	0.00	0.0
Maintenance	0.21	6.6
Analysis	0.02	0.6
Other	0.00	0.0
TOTAL DIRECT COSTS	3.04	95.2
INDIRECT COSTS		
OVERHEADS	0.15	4.8
TOTAL FIRST-YEAR ANNUAL REVENUE REQUIREMENT	3.19	100.0



CATALYST UNIT COST:	\$566/FT^3 (40,000 DM/m^3)
CATALYST DEMAND:	4600 ft^3 (130 m^3) PER 100 MW (SLAG TAP FURNACE) 3200 ft^3 (90 m^3) PER 100 MW (DRY BOTTOM FURNACE)
CATALYST COSTS:	\$26/KW (SLAG TAP FURNACE) \$18/KW (DRY BOTTOM FURNACE)

FIGURE 2-8. **GERMAN SCR CAPITAL COSTS (14)**
($1985)

FIGURE 2-9a FIGURE 2-9b

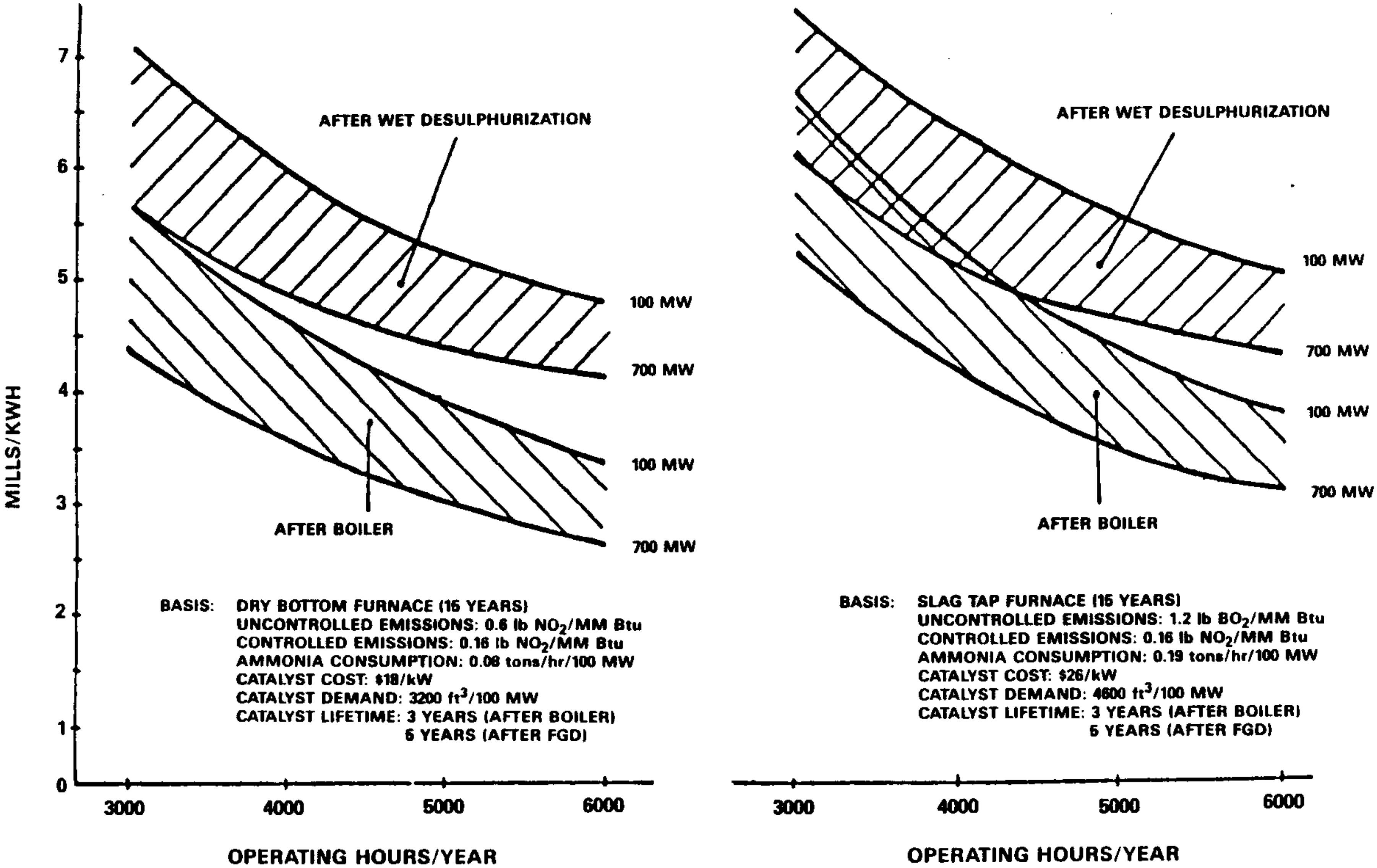


FIGURE 2-9. **COMPARISON OF GERMAN ESTIMATED ANNUALIZED COSTS OF SCR FOR "HIGH ASH" CONFIGURATION versus "COLD-SIDE" CONFIGURATION (14)**

mg/Nm^3, is projected to have a capital cost of $125/kW and an operating cost of 13.3 Mills/kWh[15].

EPRI has recently evaluated the costs of SCR and compared them with estimates for low-NO_x burners and reburning; Figure 2-10 estimates NO_x control costs for a retrofit application burning high sulfur coal. For 90% NO_x reduction, SCR is the only choice. Very long catalyst lifetimes (and low cost) are required if SCR is to be competitive at the lower NO_x control levels.

SCR applications should not be discharged simply by virtue of the costs presented above. Unique technology integration schemes could lower costs. An example is the combination of SNCR and SCR to achieve high NO_x removal levels and low NH_3 slip. The initial SNCR NO_x reduction (50 - 70%) would allow for a smaller SCR reactor volume and ammonia slip from the SNCR process can be further utilized for additional emissions reduction in the NO_x reactor. While Thermal DeNOx can be equally effective for new and existing plants, this integrated design approach may be particularly valuable (from an economic perspective) for a retrofit application and, also, in combination with the DeNO_x air heater under development in Germany. Figure 2-11 predicts the potential savings of catalyst volume by putting an SNCR system ahead of SCR[16]. The actual cost benefits of integrating the two technologies will depend on the cost of the SNCR installation relative to the SCR reactor savings.

2.9 SCR R&D Requirements

Figures 2-12 to 2-16 graphically present the SCR R&D requirements based on the previous discussion of the various technical aspects and uncertainties associated with selective catalytic reduction. The following four key areas are covered:

- o Improve existing high temperature SCR
- o Develop low temperature SCR - primarily to negate the problems associated with high SO_2 concentrations and particulate
- o Develop/improve SCR as combined with SO_2 removal (e.g. copper oxide process)
- o Perform SCR economic trade-off evaluations - R&D competition requires trade-offs of alternative designs and technologies.

The development of low-temperature SCR is apparently focusing on the use of activated charcoal and lignite coke. A German utility, Stadtwerke Dusseldorf AG, has been testing a DeNO_x process designed by a German company called Krantz[17]; this process, shown in Figure 2-17, is designed to follow an FGD process and operates in a 175 - 210^{o}F temperature range. A 6-

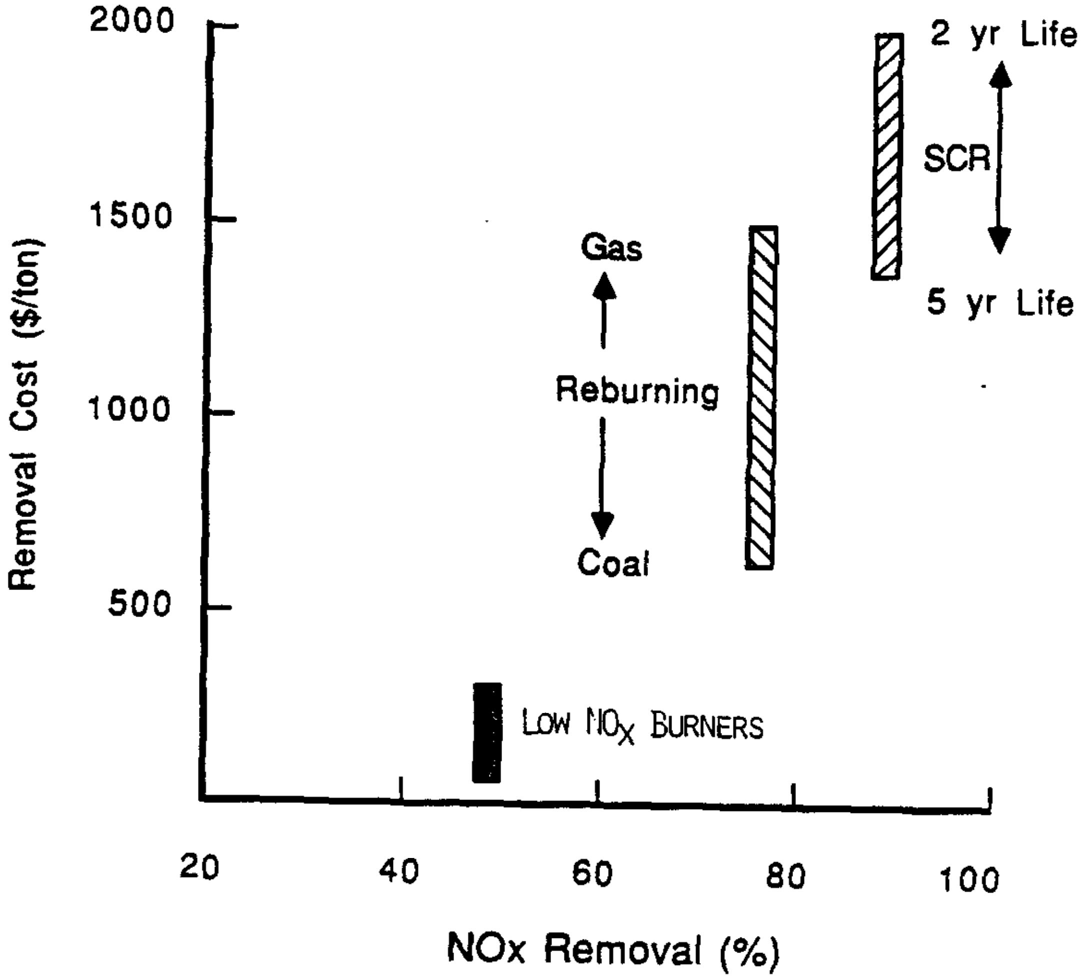


FIGURE 2-10. **RETROFIT NOx CONTROL COSTS: HIGH SULFUR COAL**

SOURCE: EPRI

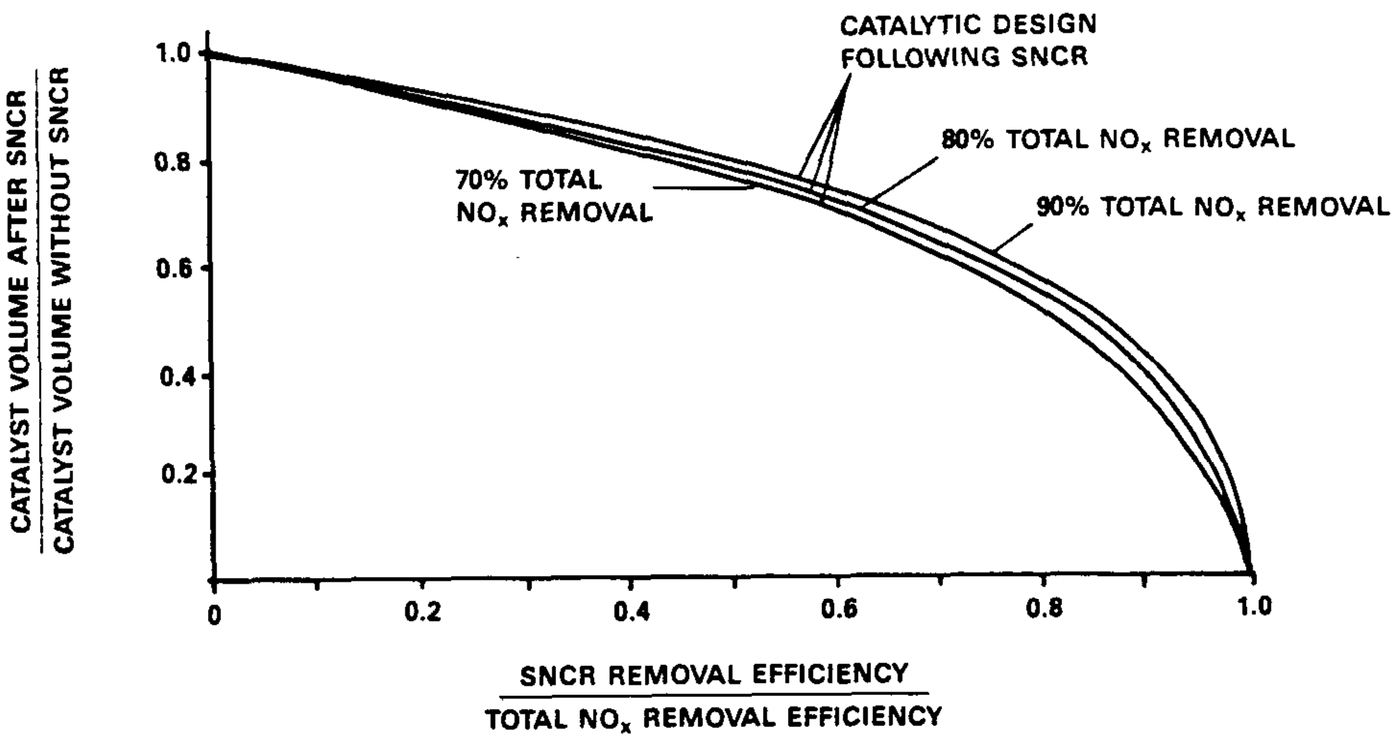


FIGURE 2-11. COMBINATION OF SNCR AND SCR NO_x CONTROL TECHNOLOGIES — EFFECT OF SNCR REMOVAL EFFICIENCY ON REQUIRED SCR CATALYST VOLUME (23).

FIGURE 2-12

SCR R&D REQUIREMENTS

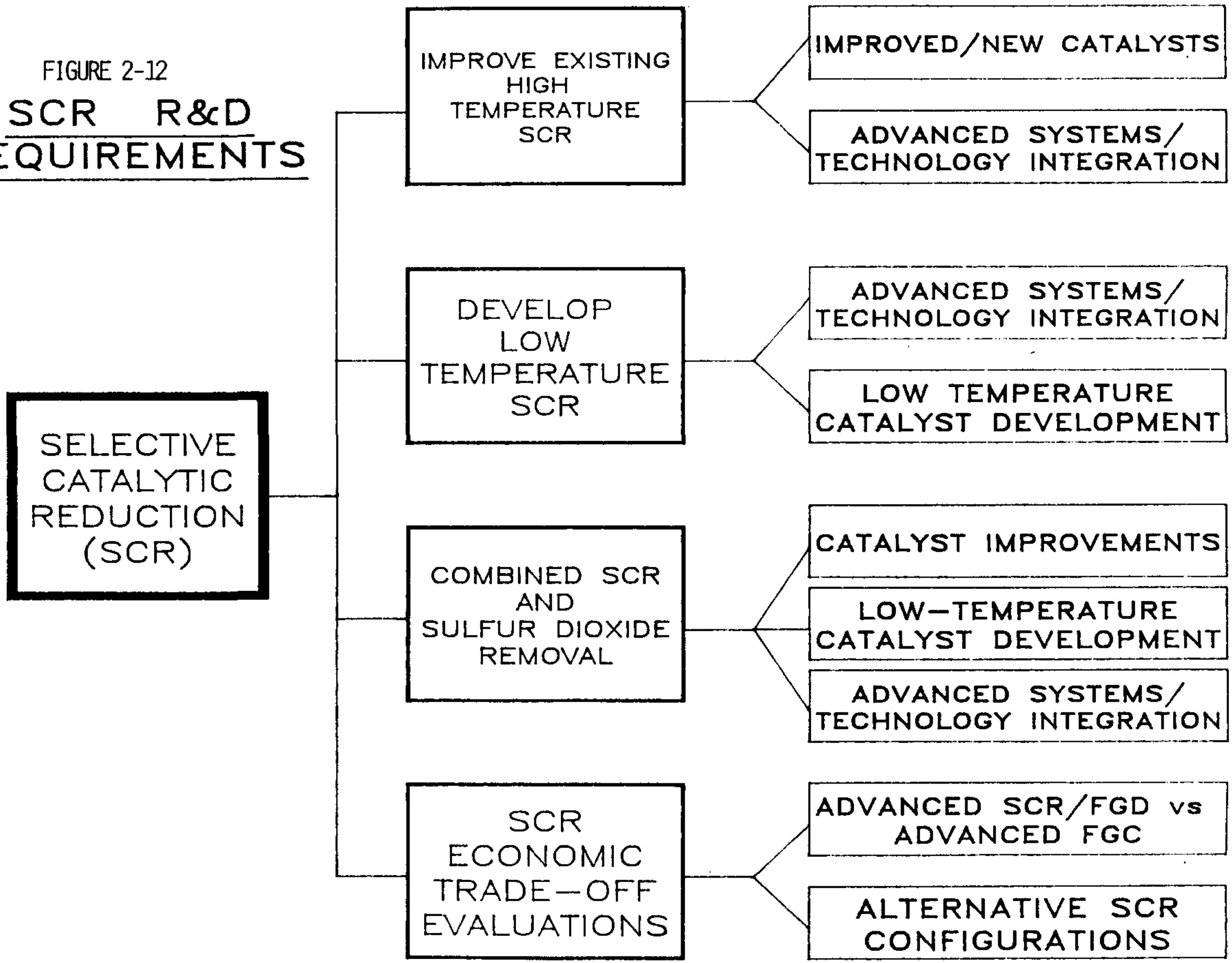


FIGURE 2-13

SCR R&D REQUIREMENTS
EXISTING HIGH TEMPERATURE SCR

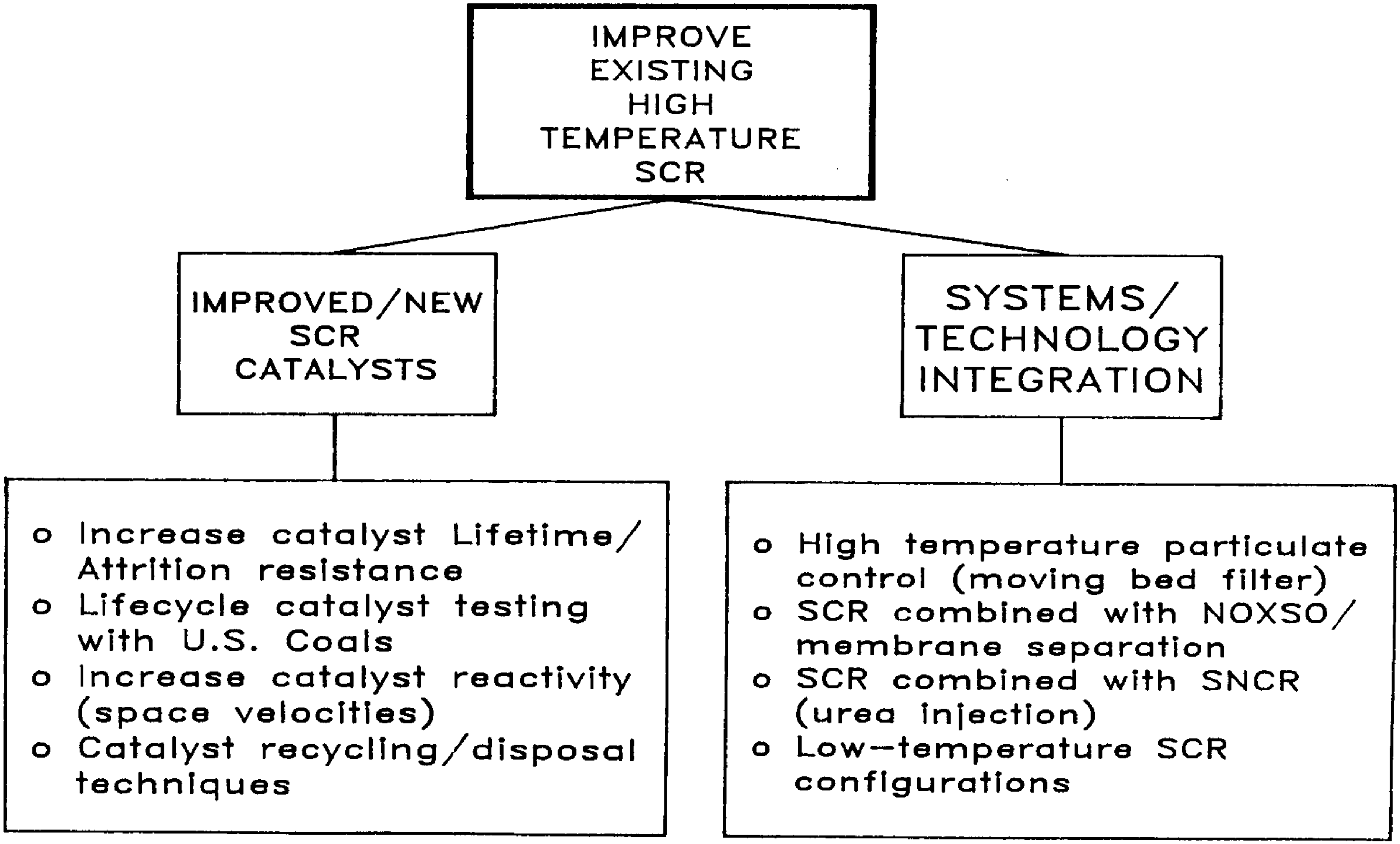


FIGURE 2-14

SCR R&D REQUIREMENTS
LOW TEMPERATURE SCR

DEVELOP LOW TEMPERATURE SCR

R&D for LOW TEMPERATURE SCR CATALYSTS

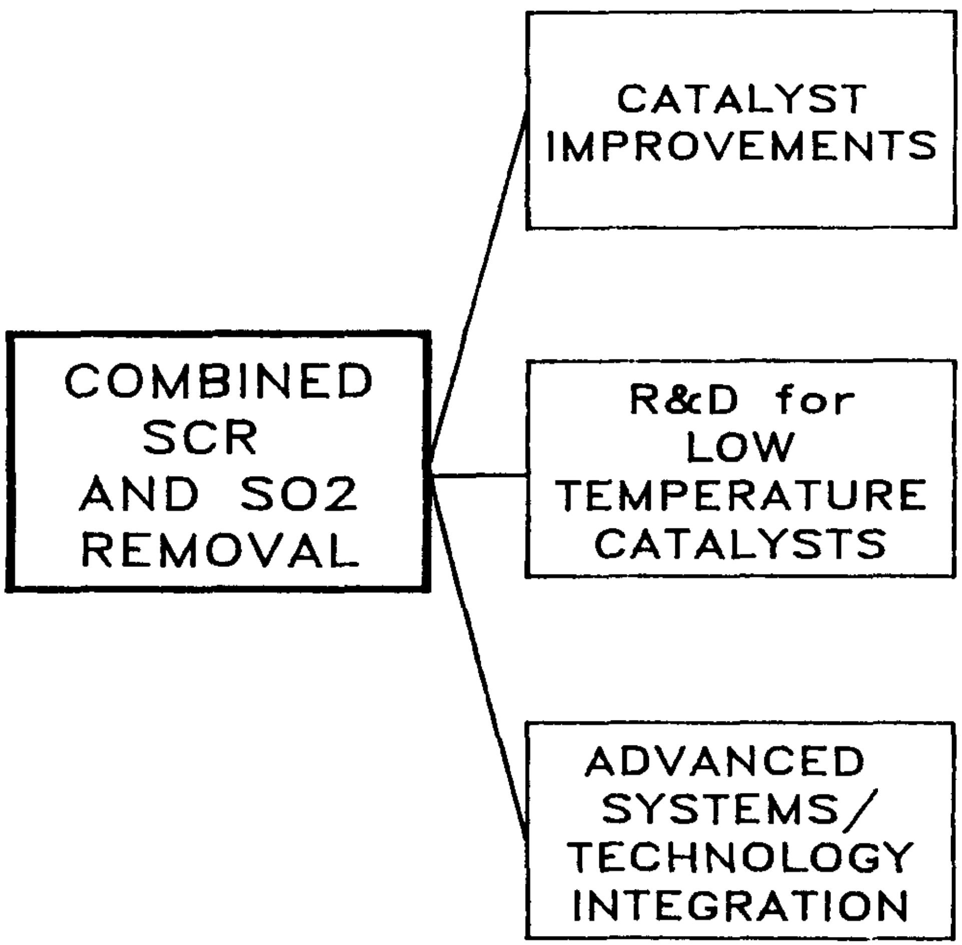
- o Evaluate potential low-temperature catalysts (CuCl2, mixed metal oxides, zeolites)
- o Establish temperature/performance ranges for key catalyst types
- o Perform reactor design studies of promising catalysts

ADVANCED SYSTEMS/TECHNOLOGY INTEGRATION

- o Low-temperature systems integration evaluations
- o Performance optimization for low-medium temperature SCR operation
- o FGD requirements to prevent ammonia salt formation

FIGURE 2-15

SCR R&D REQUIREMENTS
COMBINED SCR (NOX CONTROL) & SO2 CONTROL



- Increased lifetime
- Increased reactivity (alt. metal oxides)
- Reduced Costs (alt. catalysts support)

- Retrofit applications
- Post particulate control
  - catalyst life extension
  - limit fly ash NH3 contamination

- Low temp. operation for retrofits
- By-product conversion process integration
- Catalyst disposal issues

FIGURE 2-16

SCR R&D REQUIREMENTS
ECONOMIC TRADE-OFF EVALUATIONS

- o Hot vs. Cold SCR
  - Deterministic/probabilistic economic analyses
  - Breakeven analyses
  - Design configuration alternatives

- o SCR/Advanced Separation Technologies Analysis
  - Treatment of concentrated NOx effluent
  - Comparison with alternatives

- o SCR/Advanced FGD vs. Advanced Flue Gas Treatment Technologies
  - Breakeven analyses to determine required catalyst lifetime/cost/operating temp.

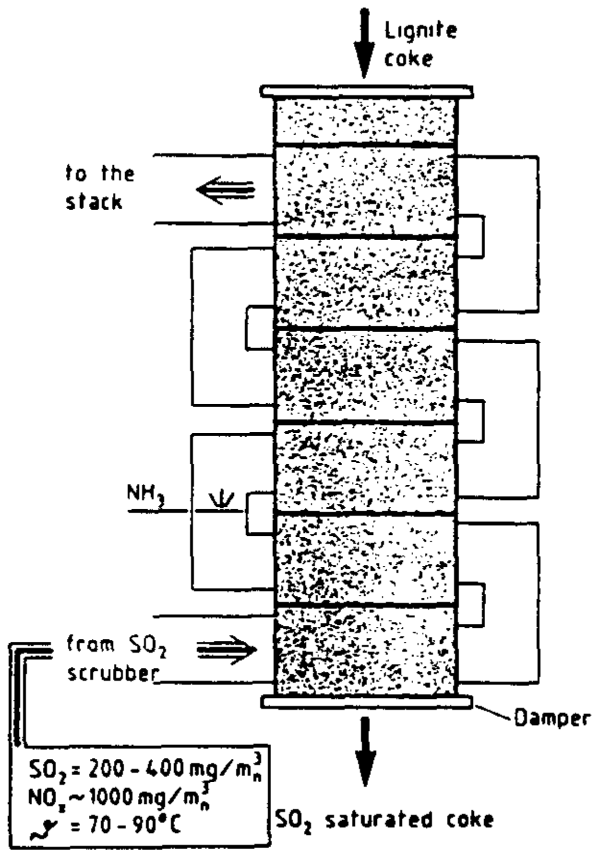


FIGURE 2-17. KRANTZ LIGNITE COKE SCR SYSTEM

stage reactor vessel utilizes lignite coke, which flows countercurrent to the flue gas, to catalyze the reaction of NO_x with injected ammonia. The lignite coke is roughly a tenth as costly as activated charcoal. Residual desulfurization takes place in the lower two beds with denitrification taking place in the upper four beds. The rate of flow of the lignite coke through the rector vessel is controlled by the SO_2 content of the flue gas exiting the second stage. The following test results have been achieved:

- 70 - 90% NO_x reductions are possible depending on the inlet NO_x concentration (the higher, the better the performance);
- Reactor dwell time is between 15 - 20 seconds for high NO_x removals and NO_x inlet concentration ranging between 400 - 600 ppm;
- Nitrates (e.g. calcium nitrates) formed in the process are broken down in-situ by sulfuric acid in the bottom stages of the reactor;
- The lignite coke is claimed to remove other pollutants from flue gas, namely, gaseous and particulate heavy metals (e.g. Hg), halogen compounds (e.g. HCl), ammonia and high molecular weight organic compounds (e.g. dioxins); and
- Combustion tests showed no difficulty in disposing of the spent lignite. Of course, ash disposal would have to account for its higher toxicity.

TABLE 2-12 [September 1988]

TECHNOLOGY NAME: Selective Catalytic Reduction (SCR)

TECHNOLOGY TYPE: Direct Reduction to N_2

TECHNOLOGY SUPPLIER: Japanese companies are primary catalyst suppliers

EMISSIONS CONTROLLED: Nitrogen Oxides

TECHNOLOGY DESCRIPTION: Catalyst is used to promote the homogeneous gas phase reduction of NO_x to elemental nitrogen by NH_3. Operating temperatures range between 550°F to 750°F for existing catalysts.

PREVIOUS EVALUATION UPDATE: June 1987 NO_x Control Overview (BRSC/SAIC)

TECHNOLOGY APPLICABILITY: Applicable to all boiler types. High sulfur coal applications may be limited to cold-side applications, after FGD. Retrofits are difficult due to operating temperature constraints, unless a cold-side configuration is selected. Cold-side configuration requires flue gas reheat to appropriate operating temperature.

DEVELOPMENTAL STATUS: Commercial for low & medium sulfur coal applications. Many applications in Japan & Germany. Applicability to high sulfur U.S. applications remains uncertain.

RAW MATERIALS, UTILITIES: NH_3, steam, electricity

BY-PRODUCTS PRODUCED: NH_3 emissions (gaseous and with fly ash), NH_3 salts

TECHNOLOGY ADVANTAGES & DISADVANTAGES:

ADVANTAGES	DISADVANTAGES
> 90% NO_x removal possible	Retrofits difficult for hot-side applications
No significant volume of waste	Emits NH_3 as secondary pollutant
Significantly less complicated than wet processes	Can form ammonia salts which plug air heater and ducts
Experience with low & medium sulfur coal applications	Sensitive to SO_3 concentration and particulates
	Catalyst disposal may be a problem due to toxicity
	Minimal high sulfur applications

TABLE 2-12 (Continued)

TECHNOLOGY NAME: Selective Catalytic Reduction (SCR)

CRITICAL DATA GAPS/POORLY UNDERSTOOD PHENOMENA:
Measurement of low ammonia concentrations in outlet flue gas has been a contributor to control problems.

Catalyst disposal options are uncertain.

SCR economic analyses have been inconsistent.

High sulfur coal applications experience is required.

Catalyst life for high sulfur applications.

RECENT DEVELOPMENTAL ADVANCES:

Improved zeolite based catalysts have been developed in Germany and the U.S.

Molecular-sieve-type catalysts may provide lower operating temperature potential and yield less SO_2 oxidation. NH_3 storage capability of the catalyst has the potential to "smooth" operation during unsteady state conditions.

Iron-oxide catalysts are being demonstrated in Germany. Such catalyst-types may be less expensive and their non-toxic nature can eliminate disposal problems. Their performance and size characteristics are key unknowns.

KEY TECHNOLOGY SUPPLIERS:

Kawasaki Heavy Industries (Japan): Joy Manufacturing, U.S. licensee

Mitsubishi Heavy Industries (Japan): Combustion Engineering, U.S. licensee

Babcock-Hitachi (Japan): Babcock & Wilcox, U.S. licensee

IHI (Japan): Foster Wheeler Energy Corporation, U.S. licensee

Hitachi-Zosen (Japan)

Norton Company (U.S.)

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3. SELECTIVE NON-CATALYTIC NO_x REDUCTION (SNCR)

3.1 SNCR Overview

The selective non-catalytic NO_x reduction process (SNCR) was invented in the early 1970's by Exxon Research and Engineering Company and called Thermal DENOx. Recent advances in the application of the process indicate that it may be better able to directly compete with the performance of SCR technology, especially for retrofit applications[1]. The process injects ammonia (or some other appropriate reducing agent) into high temperature flue gas (1600° - 2200°F) to selectively reduce NO_x to elemental nitrogen, with 1750°F being the temperature for maximum NO_x reduction. In general, the reducing agent is injected into the hot flue gas (by means of either a steam or air carrier gas if ammonia) at a point in the boiler specifically selected to provide optimum reaction temperature and residence time. If the gas temperature is too low at the point of injection, the reducing agent/NO_x reactions do not proceed fast enough, resulting in less NO_x reduction and increased ammonia slip. At temperatures above the optimum value, NH_3 will oxidize directly to NO which increases emissions, even with decreased NH_3 carryover. Since almost all testing to date has used NH_3, most of this discussion is based on use of NH_3 as the reducing agent. Alternative reagents are also discussed.

Process applications began in Japan in 1974 and NO_x reduction performance ranging up to 65% was achieved. Currently there are about 33 boilers, heaters and incinerators in Japan that make use of this technology with removal efficiencies reported to be in the range of 20 - 60% reduction for NH_3/NO_x mole ratios of 0.4 to 2.0. Since complete ammonia conversion was a problem in the original process applications, the method was used mainly on gases containing less than 100 ppm SO_2 (gas- and oil-fired applications)[2]. In the United States, a substantial number of applications have been made in California; these include gas- and oil-fired steam boilers, a utility boiler (Los Angeles Department of Water and Power's 235 MW oil/gas-fired Unit 4 boiler at Haynes Generating Station), process heaters, municipal incinerators, oil field steam generators and a glass melting furnace[1]. There is minimal experience with the process as applied to coal-fired utility boilers, although previous tests have demonstrated its effectiveness[3]. The primary concern with the coal-fired applications is the high potential of forming ammonia salts due to ammonia carryover and reaction with SO_3. However, an advantage of SNCR over SCR, in this regard, is that it will not generate additional SO_3 (from SO_2), which should place less stringent constraints on NH_3 slip.

Table 3-1 presents the technology review data form which summarizes key data for the SNCR technology.

3.2 Design Data

The original process applications involved positioning an ammonia injection grid within the boiler at the proper flue gas temperature.

TABLE 3-1 [September 1988]

TECHNOLOGY NAME: Selective Non-Catalytic Chemical Reduction

TECHNOLOGY TYPE: Direct Reduction to N_2

EMISSIONS CONTROLLED: Nitrogen Oxides

TECHNOLOGY DESCRIPTION: NH_3 OR Urea is injected into high temperature flue gas (1600°F - 2200°F) to selectively reduce NO_x to elemental nitrogen, with 1750°F being the temperature for maximum reduction. No catalysts are required. Over 70% NO_x reduction is possible and recent systems indicate greater than 80% reductions are achievable.

PREVIOUS PETC EVALUATION UPDATE: NO_x Control Technology Overview, BRSC/ SAIC, May 1985.

TECHNOLOGY APPLICABILITY: Applicable to most utility and industrial boilers and industrial incinerators and furnaces. NH_3 injection nozzle system must be custom designed for each boiler application. High sulfur coal applicability is uncertain.

DEVELOPMENTAL STATUS: Commercially applied to industrial applications in California and Japan. Utility applications are proceeding in Germany. Most applications are for fuel oil and low - medium sulfur coals.

RAW MATERIALS, UTILITIES: NH_3, steam, electricity

BY-PRODUCTS PRODUCED: NH_3 emissions (gaseous and with fly ash), NH_3 salts

TECHNOLOGY ADVANTAGES & DISADVANTAGES:

ADVANTAGES	DISADVANTAGES
High NO_x removal efficiencies have been achieved without catalysts	High NO_x removal efficiencies may be site-specific
Boiler retrofit will be significantly less complicated and less costly than most technologies	NH_3 will be emitted as a secondary pollutant and will likely be more than with SCR
Reasonable experience has been accrued for a variety of applications	Requires higher NH_3/NO_x mole ratios than SCR
Catalyst disposal or recycling is not required	Process control is likely to be difficult given changes in load which alter flue gas temperature and NO generation
Highly applicabile to cyclone boilers	Ammonia salt formation is likely, although no additional SO_3 will be produced

TECHNOLOGY NAME: Selective Non-Catalytic Chemical Reduction

CRITICAL DATA GAPS/POORLY UNDERSTOOD PHENOMENA:

Process control deficiencies may be more intolerable than with SCR

Ammonia slip restrictions for high sulfur coal applications

Ammonium bisulfate fouling tendencies for high sulfur coal applications

Urea-based SNCR reaction chemistry is not as well understood as ammonia-based SNCR

CO emissions have been shown to increase when using SNCR to reduce NO_x

Impact of ash content and changing fuel properties

RECENT DEVELOPMENTAL ADVANCES:

Urea injection, instead of NH_3, may prove to further reduce the complexity of this process type. Urea is much easier to handle than NH_3 and can be injected as a liquid, or as a lime-hydrate containing urea, with potentially better control.

Staged injection of urea with methanol claims to minimize formation of ammonia salts, reduce ammonia slip, and broaden the effective temperature window to 1500 - 1900°F.

Cyanuric acid is another alternative to NH_3 injection. While it is more expensive than NH_3, it may afford a wider operating temperature range and less sensitivity to oxidation.

Use of wall injectors for the injection of the reducing agent has improved mixing with the flue gas

A German application has shown NO_x reduction of 80% with an NH_3/NO_x ratio of about 1.6 and a commensurate ammonia breakthrough of less than 10 ppm.

KEY TECHNOLOGY SUPPLIERS:

Exxon Research and Engineering: Thermal DeNOx NH_3-based SNCR

Fuel Tech, Inc.: NOxOUT urea-based SNCR

Fossil Energy Research Corporation: Lime-urea hydrate for combined NO_x/SO_x

EMCOTEK Corporation: Two-stage DeNOx process using staged injection of urea and methanol

Location of the grid is critical to achieving optimum NO_x reduction performance; typically, however, the optimum position is inaccessible and the operating environment can be corrosive and erosive which causes grid maintenance problems. However, within the past several years, the process has been modified to replace the injection grid with wall injectors[1]. These injector nozzles are simple and relatively inexpensive, but require careful design and placement to yield optimum NO_x reduction. Often, little modification of the boiler is required to locate and install the nozzles. An important aspect of the process application design is the proper modeling of the reaction kinetics and ammonia distribution within the boiler injection zone. Exxon has developed a kinetics model of the process which correlates to within $\pm 7\%$ of experimental data, and it is coupled to a 3-dimensional, turbulent flow modeling technique to predict the design performance for different geometries and flow conditions. The modeling technique has been validated by field testing at a 200 ton/hr oil- and gas-fired power boiler in Kawasaki, Japan; at 80% load the model predicts 67.5% NO_x reduction, while 70% was actually achieved in the field tests. Ammonia breakthrough in these tests ranged between 30 and 90 ppm (very high compared to SCR).

3.3 Recent Test Results (NH_3 Reducing Agent)

The most recent installations of the newer SNCR technology are in Germany where two coal-fired boilers have been retrofitted; they are both cyclone-type applications located, respectively, at the 55 MW(e) unit of the Mainz-Weisbaden Power Plant and the 85 MW(e) unit of the Marl Power Plant. The following discussion applies only to the Mainz-Weisbaden retrofit. This particular unit generates NO_x emissions of about 840 ppm (1.4 lb/MMBtu), and, without retrofit controls, the 18 year-old boiler would have been shut down after an additional 30,000 hours for being out of compliance with regulations[4]. The design of the boiler offers the following favorable conditions for application of the SNCR process: 1)flue gas temperature of about 1832°F (1000°C) at a convenient location for nozzle installation, 2)a gas residence time of 0.6 seconds (more than adequate), and 3)a relatively low gas cooling rate of 252°F/sec (140°C/sec). However, on the negative side, the temperature differential over the boiler cross-section ranges between 108 - 180°F (60 - 100°C). In spite of the latter plant operating characteristic, Exxon guaranteed the Thermal DeNOx performance at 70% NO_x removal with less than 5 ppm NH_3 breakthrough while operating at full boiler load. Some of the test results at full boiler load are shown in Figure 3-1; NO_x reduction of 90% can be attained with an NH_3/NO stoichiometry of about 2.4 and a carrier momentum value of 3600 ft-lb/sec^2 (500 m-kg/sec^2), resulting in an ammonia slip of less than 20 ppm. These results also indicate the importance of NH_3/flue gas mixing quality by comparing tests conducted at two levels of carrier gas momentum (i.e. product of the mass of injected steam and the velocity at the nozzle tip). NO_x reduction efficiency falls significantly and NH_3 breakthrough increases as carrier gas momentum is reduced. Similar NO_x removal efficiencies can be achieved at part load operation, but NH_3 slip increases due to the lower flue gas temperatures at the NH_3 injection location. For applications in which load swings may be substantial, and high NO_x removals are also required

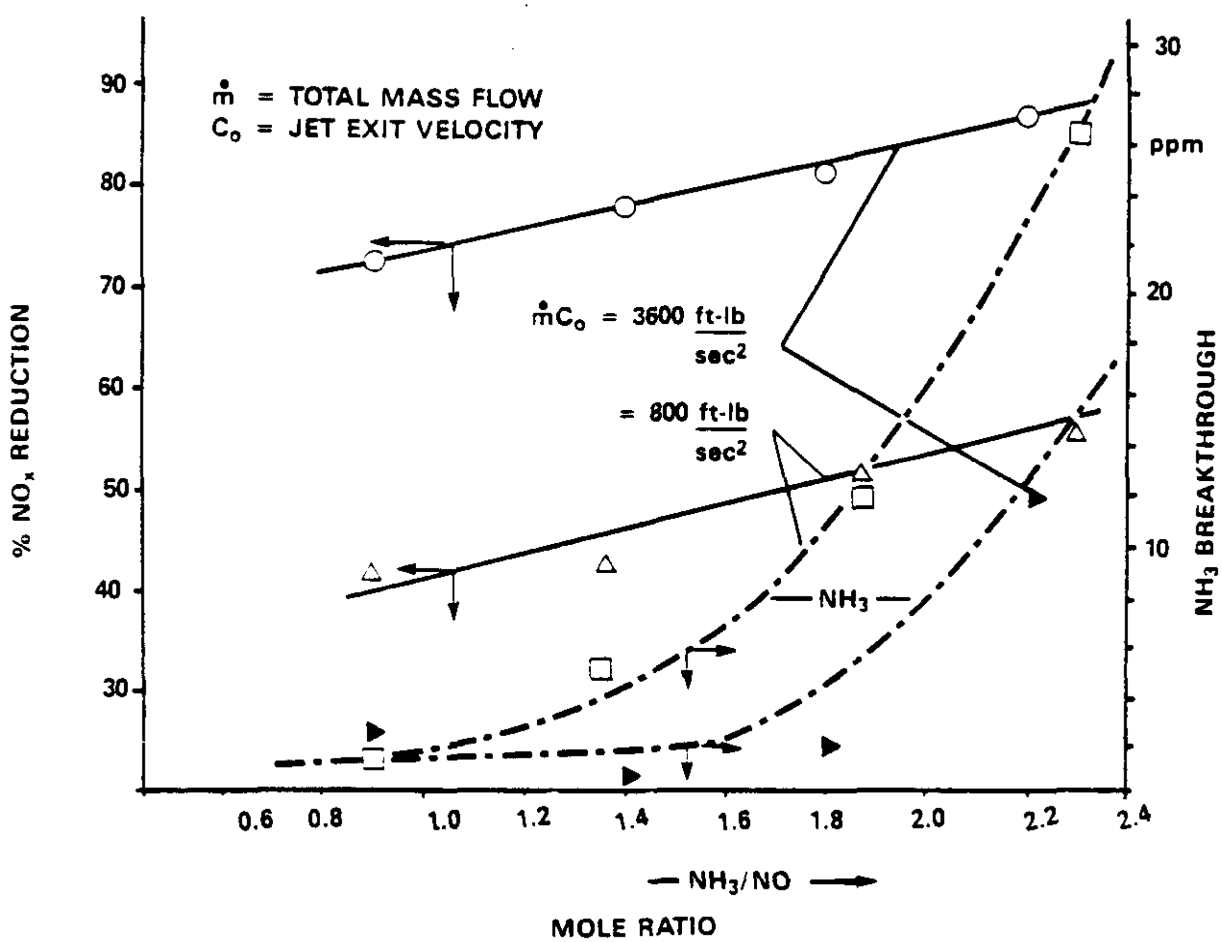

FIGURE 3-1. SNCR NO_x REDUCTION RESULTS AT MAINZ-WIESBADEN POWER PLANT: NO_x REDUCTION EFFICIENCY AND NH_3 BREAKTHROUGH @ FULL BOILER LOAD (23).

at reduced loads, multiple sets of wall injectors could be used for tracking the optimal gas temperature[5] (given that gas residence time is not a limiting factor). Testing at this plant is continuing so as to minimize the quantities of consumables and to help determine the relationship between NH_3 slip and its effects on air heater plugging.

Ammonia breakthrough is clearly the most critical aspect of applying this technology to a coal-fired plant. Because it depends upon the interaction of so many design and operating factors, ammonia slip must be evaluated for particular combustion equipment; the placement of the ammonia injection nozzles to achieve a desirable time-temperature relationship and the mixing effectiveness of these nozzles are key factors in minimizing NH_3 breakthrough. For suitable applications, such as the previously discussed retrofit, the Thermal DeNOx process can be designed to meet very low NH_3 slip requirements, while for some applications the combination of high NO_x removal and low NH_3 slip are incompatible because of peculiar boiler design and operating characteristics. Once a design specification has been established, Exxon claims that the use of chemical equilibrium data for ammonium bisulfate, ammonia sulfate and SO_3, coupled with a "low fouling assessment criteria" developed from previous plant experience, should permit an assessment of bisulfate fouling tendencies. However, even if the fouling problems are curtailed, any excess NH_3 concentrations may still cause waste disposal problems of ash and FGD wastewater.

3.4 Alternative SNCR NO_x Reducing Agents

Alternatives to the use of NH_3 as the NO_x reducing agent have been and are continuing to be investigated, particularly urea (NH_2CONH_2) and cyanuric acid ($NC{*}CH(NO_2){*}CONH_2$). Urea injection was initially developed at the bench-scale in 1976 by KVB, Inc. under the sponsorship of EPRI[6]. As developed, the urea is sprayed directly into the combustion gas as an aqueous solution. NO_x reduction has been shown to take place at temperatures ranging between 1400°F to 2000°F. The exact chemical pathways associated with the urea reagent are not known; urea thermocracking and decomposition leads to the production of NH_i species which act on the NO_x. It is assumed, based on the urea chemical composition, that two moles of NH_2 are produced per mole of urea.

The most important variables that influence process performance are:

- Urea/NO mole ratio (stoichiometric molar ratio = 0.5)
- Initial NO concentration
- Urea injection variables: atomizer type, injection location, and degree of atomization
- Urea concentration in solution.

In 1985 a large-scale test of the urea injection process was conducted at San Diego Gas and Electric's oil-fired Encina Generating Station. The field assessment was co-sponsored by Fuel Tech which has been licensed by

EPRI to offer the technology commercially under the trade name NO_xOUT. The test results are shown in Figure 3-2[6]; 50% NO removal was achieved at stoichiometric values of urea and 70% NO removal was attained when stoichiometric values were doubled (for the oil-fired case). Laboratory data indicates a dependence on initial NO concentration; coal-fired applications should, therefore, likely show higher NO reductions than are reported by this test program. The tests showed that NH_3 is a by-product of urea injection; the injection of a stoichiometric amount of urea yielded NH_3 slip ranging between 10 - 50 ppm. No HCN or nitrosamines were measured.

Other tests with urea injection were conducted by Fuel Tech in 1987 on a 55 MW(e) coal-fired utility boiler in Sweden[7]; 70% NO_x reduction was achieved with less than 10 ppm ammonia slip being measured.

Figure 3-3 shows the results of some recent test data from Fossil Energy Research Corporation for an SNCR process utilizing urea by incorporating it in a lime-hydrate.

EMCOTEK Corporation offers another variation of urea injection by combining it with second stage injection of methanol. The methanol is used to reduce ammonia slip, ammonia salt deposits and to broaden the application temperature window (1500 - 1900°F)[8].

The virtues of using urea are as follows:

- Moderately high NO_x removal is possible
- Each mole yields two moles of NH_2 for reducing NO_x
- Urea is easy and safe to handle in dry or anhydrous forms
- May be easier to inject as a liquid into the gas stream
- Significant quantities of Urea are produced in the U.S. (>7 million tons/year)
- Possibly less expensive than ammonia injection and storage
- Can be combined with lime (hydrate or slurry) for combined NO_x/SO_x removal.

Drawbacks to the use of Urea are:

- CO_2 is evolved
- Reaction chemistry is not as well understood as NH_3
- Secondary emissions are generated in the form of NH_3
- Significant boiler turndown and cycling will negatively impact control performance
- CO emissions increase.

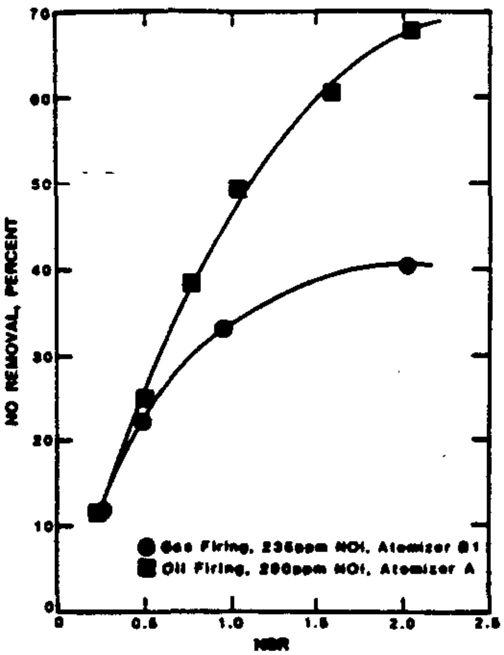

Figure 3-2a NO Removal as a Function of NSR - 110 MW

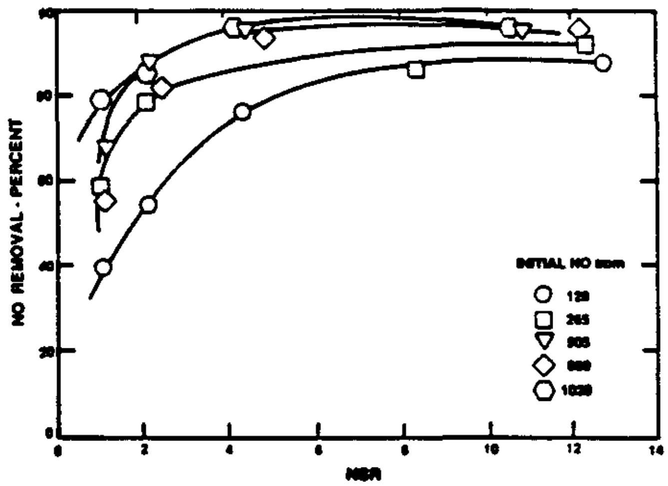

Figure 3-2b Effect of Initial NO Concentration on NO Removal - Laboratory Data

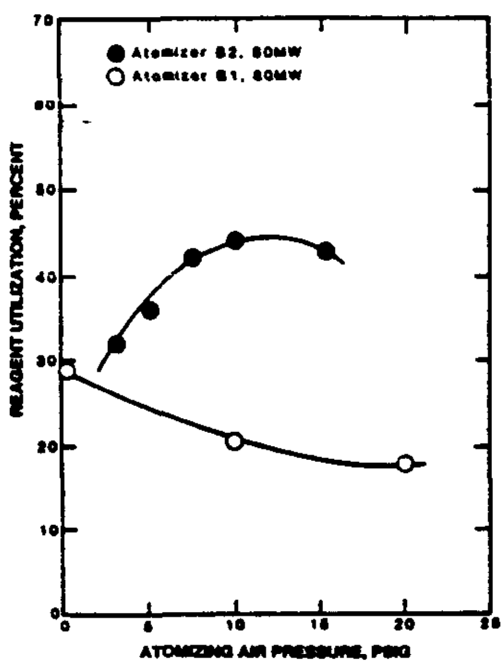

Figure 3-2c Effect of Atomization Pressure on Utilization

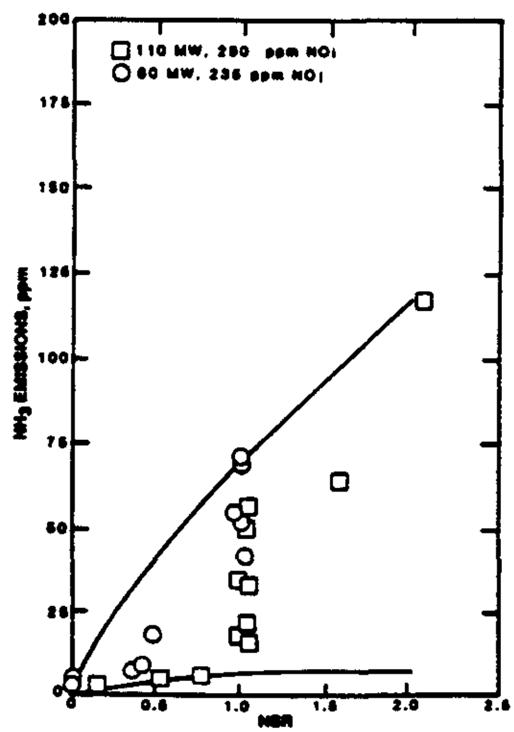

Figure 3-2d NH_3 Emissions Resulting from Urea Injection During Fuel Oil Firing

FIGURE 3-2. FULL-SCALE UREA INJECTION TEST RESULTS

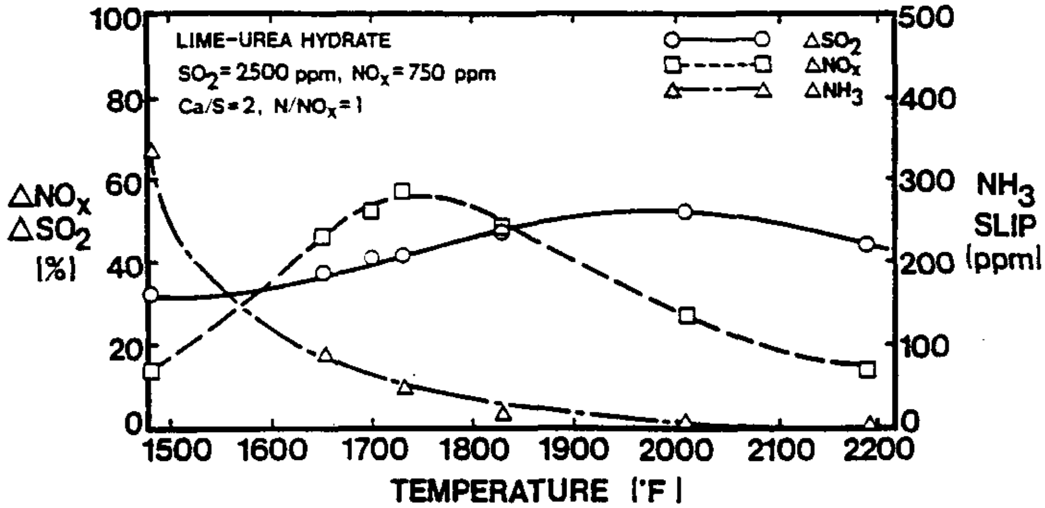

FIGURE 3-3A

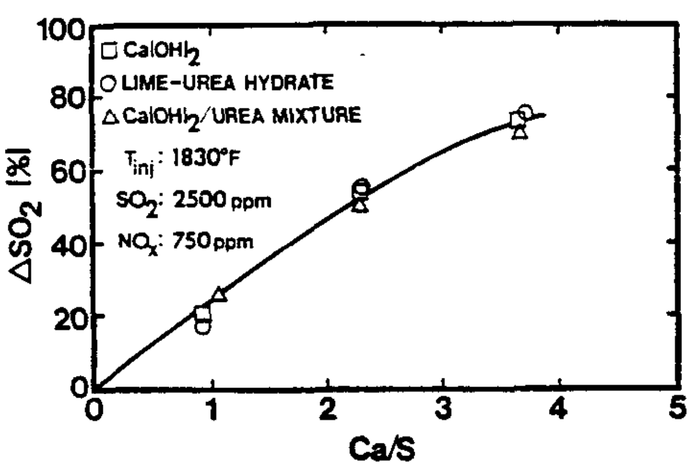

FIGURE 3-3B

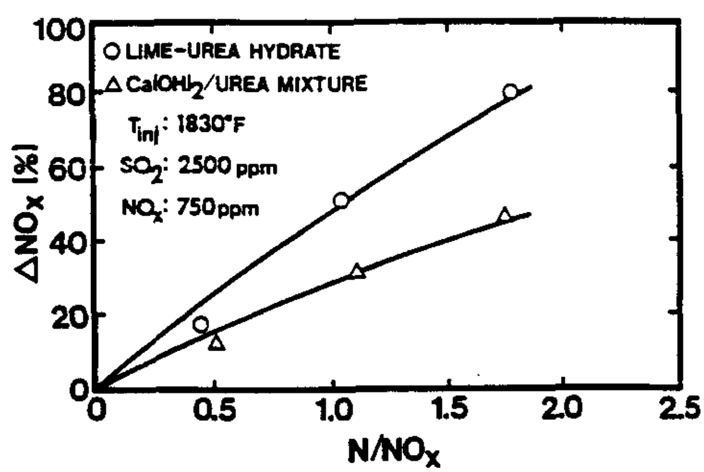

FIGURE 3-3C

FIGURE 3-3. PILOT-SCALE TESTS WITH LIME-UREA HYDRATES AND MIXTURES

Another SNCR reducing agent, Cyanuric acid ($NC*CH(NO_2)*CONH_2$), has also been found to be as effective as NH_3 for NO_x reduction in the SNCR process. Advantages include:

- o Effective as NH_3 for NO_x reduction
- o Potentially less oxidation sensitivity
- o Potentially operates within wider temperature range.
- o Highly soluble in water.

Potential drawbacks include:

- o More expensive than NH_3
- o Reaction chemistry is not well understood
- o Secondary emissions are uncertain.

3.5 SNCR Economics (NH_3-based SNCR)

Cost estimates have been developed by Exxon which compare the "new" and "old" SNCR designs with SCR for similar 500 MW utility applications[1]; these are presented in Table 3-2. The cost data indicates that the investment costs for the improved technology are 45-55% of the older technology and is approximately 3 to 4 times more cost effective than SCR. These cost estimates apparently assume an application that is well suited to the use of SNCR technology and, therefore, minimize its cost. However, even if the process was technically limited to 50 - 60% removal, for example, there may be economic benefits associated with integrating it with SCR to achieve high NO_x removal levels and low NH_3 slip. The initial NO_x reduction would allow for a smaller SCR reactor volume and ammonia slip from the SNCR process can be further utilized for additional emissions reduction in the NO_x reactor. While Thermal DeNOx can be equally effective for new and existing plants, this integrated design approach may be particularly valuable (from an economic perspective) for a retrofit application and, also, in combination with the SCR technology. Figure 2-11 predicts the potential savings of catalyst volume by putting an SNCR system ahead of SCR[4]. The actual cost benefits of integrating the two technologies will depend on the cost of the SNCR installation relative to the SCR reactor savings.

3.6 SNCR R&D Requirements

Significant R&D has been performed on SNCR during the last 15 years and has resulted in the German installations and several recent U.S. demonstrations of the urea injection technology. The key to applying the technology is proper engineering of the injection nozzles and control

TABLE 3-2

COST COMPARISON BETWEEN ORIGINAL AND IMPROVED SNCR TECHNOLOGY AND SCR TECHNOLOGY FOR 500 MW COAL-FIRED PLANT

TECHNOLOGY	$/KW[1]	NO_x = 300 PPM (0.4 LB/MMBtu) MILL/KWH[2]	$/TON NO_x[3]	$/KW[1]	NO_x = 600 PPM (0.8 LB/MMBtu) MILLS/KWH[2]	$/TON NO_x[3]
Old SNCR (70% NO_x Removal)	23.6	3.07	1940	34.3	5.26	1660
New SNCR (80% NO_x Removal)	13	2.03	1140	15.5	2.94	820
KHI (SCR) (90% NO_x Removal)	-	9.86	4860	-	12.53	3080

NOTES
1. Total capitalinvestment.

2. Annual revenue requirements (Capital and O&M).

3. Annual revenue requirements put on the basis of lb NO removed.

systems; site-specific gas velocity and temperature measurements are required and boiler flow modeling enhances design optimization. This technology, in its various forms, is thus on the verge of commercialization.

Additional R&D may be required as follows:

- High sulfur coal applications demonstration
- Identification and quantification of secondary emissions: CO, amines, etc.

SECTION 3 - REFERENCES

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3-3. Varga, G.M., et al., "Applicabilityof the Thermal DeNOx Process to Coal-Fired Utility Boilers", EPA 600/7-78-079, March 1979.

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4. ELECTROCATALYTIC NO_x REDUCTION - SOLID ELECTROLYTE DECOMPOSITION CELLS

4.1 Technology Overview

Solid electrolyte decomposition cells reduce gaseous compounds containing oxygen at the cell cathode, while forming oxygen at the anode via selective transport of the oxygen ions through a solid electrolyte of high oxygen-ion conductivity. Figure 4-1 depicts the concept for using these electrolytes for an emissions control system. NO_x removal depends on the relative reaction rates between the NO_x and other oxygen-containing gaseous species in the flue gas at various temperatures and cell voltages. The fundamentals of the technology date back to 1899 when Nernst discovered that oxygen could pass through stabilized zirconia, a solid electrolyte, by the process of ion conduction. He predicted and confirmed that the potential difference across the electrolyte, caused by the difference of partial pressures of oxygen between the two sides, was given by the expression[1]:

$$E = (RT/ZF) \times \ln(P_2/P_1)$$

Where,

- E = electrical potential, volts
- R = universal gas constant, 8.314398 J/mole-K
- T = temperature, K
- Z = charges/molecule ($Z = 4$ for O_2)
- F = Faraday constant, 9.648679×10^4 amp-sec/equiv. mole
- P_1 = partial pressure of oxygen on the supply side of the solid electrolyte, N/m^2 (Pascal)
- P_2 = partial pressure of oxygen on the discharge side of the solid electrolyte, N/m^2 (Pascal)

The Nernst equation is the basis for the operation of a solid electrolyte cell "oxygen pump" used as an advanced flue gas treatment process to reduce NO_x (and SO_x). The actual voltage required to conduct the oxygen ions through the electrolyte will be greater than that predicted by the Nernst equation since the solid electrolyte also has an internal resistance to overcome; the electrolyte resistance is a function of material resistivity (ohm-cm) and the electrolyte thickness[2]. In most applications, the Nernst voltage will be negligible in comparison to the ohmic voltage. The upper limit to the applied voltage prevents the risk of damaging the electrolyte by stripping oxygen out of the ionic bonds[2].

The electrolyte cell size is determined by establishing the minimum surface area that will satisfy the requirements for current density, gas residence time and mass transfer characteristics.

Table 4-1 presents the completed technology review data form for this technology.

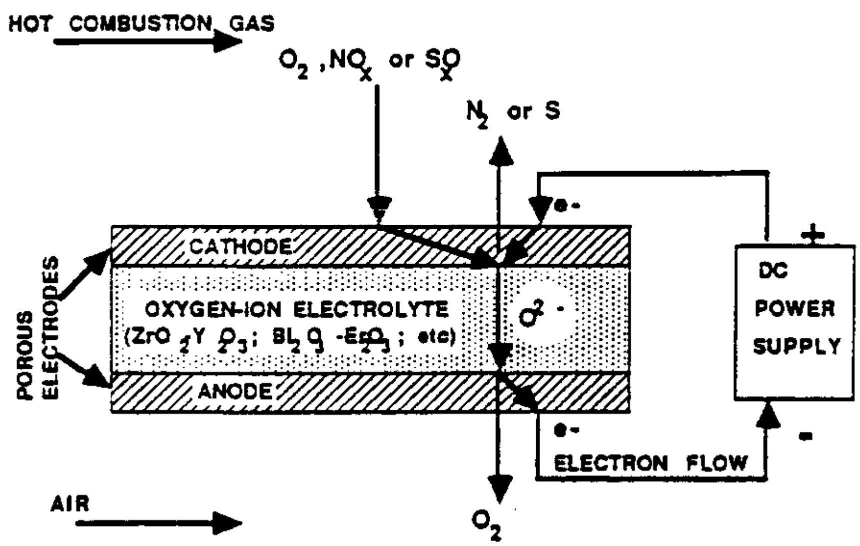


FIGURE 4-1. SCHEMATIC REPRESENTATION OF SOLID OXIDE ELECTROLYTE CELL FOR FLUE GAS CLEANUP.

TABLE 4-1 [DATE: Sept. 1988]

TECHNOLOGY NAME: Electrochemical Reduction - Solid Electrolyte Decomposition Cells

TECHNOLOGY TYPE: Direct Reduction to N_2

EMISSIONS CONTROLLED: NO, NO_2, SO_2, SO_3

TECHNOLOGY DESCRIPTION: Technology is based on development of solid-state electrochemical cells which reduce gaseous compounds containing oxygen at the cell cathode, while forming oxygen at the anode via selective transport of the oxygen ions through a solid electrolyte. The solid electrolyte material, which acts as an "oxygen pump", has been made of a stabilized zirconia and the electrodes of various materials (nickel, silver, copper). Reduced sulfur and nitrogen remain in the flue gas. Sulfur is condensed out at an appropriate temperature.

PREVIOUS PETC EVALUATION UPDATE: 4th Annual Contractor's Conference - IGR Enterprises Program review, August 1988

TECHNOLOGY APPLICABILITY: Potentially applicable to all boiler types. Operating temperature may limit particular utility and industrial boiler applications.

DEVELOPMENTAL STATUS: Bench-scale development of the solid-state electrolyte and electrodes for flue gas applications has been sponsored by PETC since September 1985. The technology still remains at this level of development.

RAW MATERIALS, UTILITIES: fuel gas or fuel oil, electricity

BY-PRODUCTS PRODUCED: elemental sulfur, elemental nitrogen, elemental O_2

TECHNOLOGY ADVANTAGES & DISADVANTAGES:

ADVANTAGES	DISADVANTAGES
No reagents or sorbents required	High operating temperatures may be required to achieve high NO conversion
Useful by-products are produced	
Dry process - no water requirement	High temperature, high efficiency particulate control required to protect cells against plugging
No secondary pollutants	
	Reoxidation of gaseous elemental sulfur may pose problems as well as corrosion by sulfur
	Potential electrochemical transport of flue gas excess oxygen will significantly increase energy use

TECHNOLOGY NAME: Electrochemical Reduction - Solid Electrolyte Decomposition Cells

CRITICAL DATA GAPS/POORLY UNDERSTOOD PHENOMENA:
Zirconia-based solid electrolyte must be operated above 600°C (1112°F) for significant NO_x conversion - lower temperatures (400°C - 450°C) are desired to locate process downstream of a power plant economizer without flue gas reheat: zirconia electrolyte must be altered/other materials must be evaluated.

Electrode materials have not had long life during Ceramatec experimental program due to sulfidation - significant work will be required to obtain desired characteristics.

Plugging, fouling and erosion of the electrolyte (by particulate/trace elements) could prevent use of the technology even if the electrochemical cell is successfully developed; significant attention must be paid to the particulate control requirements.

Collection of the sulfur vapor must be evaluated as well as its corrosion potential. The Ceramatec/VSM integrated design configuration should be critically reviewed.

RECENT DEVELOPMENTAL ADVANCES:
Ceramatec and Stanford tests showed that NO_x can be reduced under conditions of temperature and voltage that will not significantly decompose CO_2, O_2, and SO_2. IGR tests claim low oxygen consumption rates.

Utilizing a purge gas at the anode reduces the oxygen partial pressure; oxygen buildup can reduce the efficiency of oxygen transport through the electrolyte cell.

Partially reduced zirconia significantly enhances oxygen transport through the electrolyte cell.

IGR/Helipump will be evaluating a ceria-based porous, flow-through electrolyte which is stabilized with gadolina and a bipolar stack design. A design for a 10 CFM demonstration unit has been completed and construction is in progress. Cottrell Environmental Sciences (under a subcontract to IGR) has designed and is fabricating a high temperature particle collector for the demonstration unit.

KEY TECHNOLOGY SUPPLIERS & R&D ORGANIZATIONS:

Ceramatec/VSM: PETC R&D contract (DE-AC22-85-PC81003), September 1985-June 1986.

IGR Enterprises/Helipump Inc.: Follow-on contract to previous Ceramatec work (DE-AC22-87PC79855), July 1987 - May 1989. IGR & Helipump are providing similar support to METC for the Heat Engine program.

Stanford University Chemical Engineering Department (METC & PETC).

4.2 Solid Electrolyte Material

4.2.1 Zirconia-based Electrolyte

Stabilized, or doped, zirconia (zirconium oxide or ZrO_2) is an electrolyte that has been found to possess most of the desired properties required for solid electrolyte applications: high oxygen ion conductivity, low porosity, chemical stability, good phase stability and high thermal shock stability. When zirconia is doped with divalent or trivalent cations (such as Y_2O_3) which have a similar size to the Zr^{4+} ion, oxygen vacancies are created within a distorted fluorite cubic crystal structure. These vacancies compensate for the charge difference between the zirconia ions and the doping ions and, therefore, the zirconia behaves much like a semi-conductor, except that oxygen ions (rather than electrons) move from one vacancy to another.

Application of the solid electrolyte cell to flue gas emissions control is based on the theory that the thermodynamic and kinetic conditions exist at which NO_x (and SO_x) molecules will decompose when they contact a hot electrolyte surface and that the resulting oxygen ions will be transported through the cell (due to an applied voltage) such that they cannot recombine with the nitrogen or sulfur ions. Figure 4-2 depicts the potential reactions in a solid electrolyte cell. Since the NO_x (and SO_x) reduction reaction rate follows the Arrhenius form ($K = Ae^{-E/RT}$), the reduction reaction rate increases with increasing temperature. Kinetics studies for the zirconia-based electrolyte indicate that the cell temperature should be greater than 750°F (400°C) to allow pollutant removal in a reasonably sized reactor vessel. NO_x-only removal depends on the relative reaction rates between the NO_x and other oxygen-containing gaseous species in the flue gas at various temperatures and cell voltages.

The Ceramatec test program resulted in the following conclusions regarding the use of stabilized zirconia:

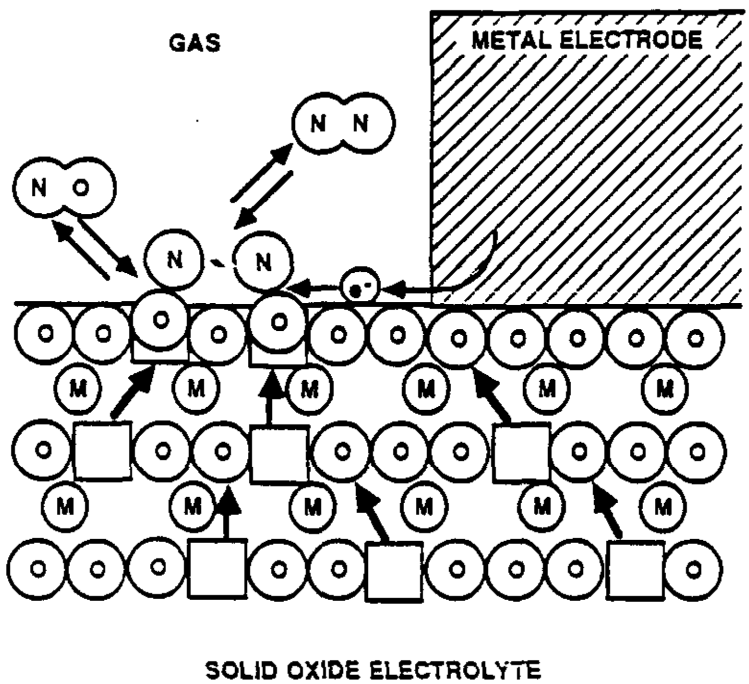
- **The solid electrolyte decomposition cell is most selective for NO_x and then SO_x.** 1 - 2 volts are required for temperatures between 600 - 800°C.

- **Zirconia-based solid electrolyte must be operated above 600°C (1112°F) for significant NO_x/SO_x conversion rates and below 800°C to avoid other undesirable reactions. CO_2 and H_2O require higher temperatures for decomposition.**

- NO_x can be reduced under conditions of temperature and voltage that will not significantly decompose CO_2, and SO_2. Figure 4-3 shows the temperature range of decomposition for the key oxygen-containing gases for a 0.95 volt potential difference. No data was included for higher voltages.

- Oxygen in the flue gas is removed at the same temperature and voltage range as SO_x and NO_x. This increases the power requirement for the cell operation.

$$O_2 + 4e \underset{anode}{\overset{cathode}{\rightleftharpoons}} 2O^{2-} \qquad\qquad O_2 + 4e' + 2V_O^{\circ\circ} \underset{anode}{\overset{cathode}{\rightleftharpoons}} 2O_O^x$$



O represents an oxygen ion in an oxygen lattice site

□ represents a vacant oxygen lattice site (F-center)

M represents a metal ion (Zr^{4+}, Bi^{3+}, etc) in a metal lattice site

FIGURE 4-2. MODEL OF THE CATHODIC ELECTRO-REDUCTION OF NO

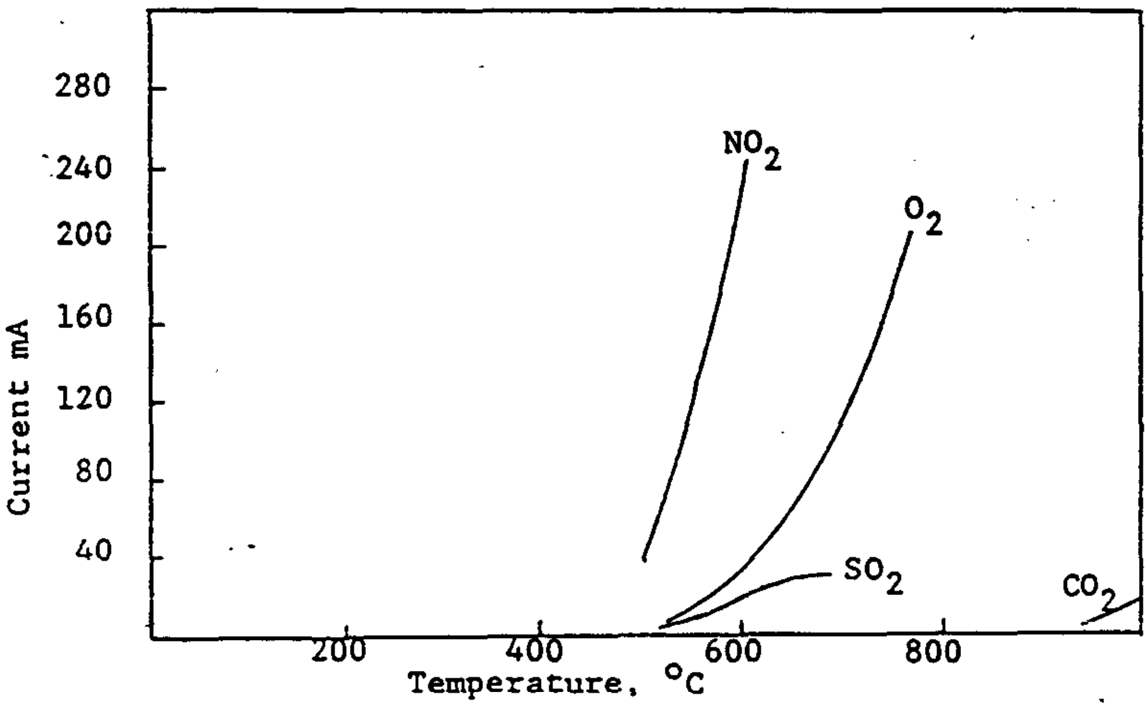


FIGURE 4-3. Temperature range of decomposition for various gases with the bench-scale zirconia cell at an applied voltage of 950 mV (tests conducted with a silver electrode on the ID and a platinum electrode on the OD).

- o Utilizing a purge gas at the anode reduces the oxygen partial pressure; oxygen buildup can reduce the efficiency of oxygen transport through the electrolyte cell.

- o Partially reduced zirconia significantly enhances oxygen transport through the electrolyte cell. Figure 4-4 compares the "blackened" zirconia with the standard zirconia electrolyte cell. It is suggested that the partially reduced zirconia surface contains F-centers (trapped electrons) and that these oxygen-ion deficient centers provide the active sites that are responsible for the catalytic enhancement[3]. Note that the NO concentration tested is 40000 ppm which is two orders of magnitude higher than would be seen in actual flue gas. The effect of NO concentration on cell performance was not included in test results, but, since this is a positive-order reaction, the concentration will have a significant impact on the reaction rate at a particular temperature and voltage.

Tests at Stanford University appear to reinforce Ceramatec's results[3]. They found that it was possible to reduce NO and SO_2 at high electrocatalytic rates and that "blackening" increased the rates by 2 orders of magnitude. NO has been found to be preferentially reduced compared to O_2 with the rate being 5 to 10 times as fast. Both kinetic data and surface analysis show that the electrolyte provides the electrocatalytic sites, not the metal electrodes; therefore, they claim that inexpensive metals can be utilized for the electrodes and a large ratio of electrolyte to electrode surface area is desirable.

4.3 Other Electrolyte Materials

A key aspect of PETC's current contract with IGR/Helipump is the investigation of alternative electrolytes to achieve higher electrolytic conductivity and lower temperature operation. The former goal is necessary to minimize the size of the electrocatalytic reactor(s). The latter goal is desired so that the device can be placed in power plant and industrial boiler applications downstream of the super heat and reheat heat transfer surface and to negate the need for flue gas reheat to the system operating temperature. IGR will be evaluating the use various electrolyte compositions, including gadolina stabilized ceria and baria stabilized bismuth; IGR claims that these materials may have electrolytic conductivities as much as 50 times greater than the yttria stabilized zirconia used in the research conducted by Ceramatec. IGR also claims that their proprietary electrocatalysts minimize parasitic oxygen reduction.

In addition to stabilized zirconia, Stanford evaluated Er_2O_3-stabilized Bi_2O_3 (ESB, 20 mole% Er_2O_3). Their fluorescence spectroscopic studies indicate that this material, while different from zirconia, has similar types of oxygen vacancies. ESB appears to perform similarly to the zirconia electrolyte, with better performance at lower temperatures (400 700°C). However, ESB is not as thermodynamically stable as the zirconia; sulfidation of the bismuth occurs. Also, both O_2 and SO_2 are dissociated simultaneously, without selectivity.

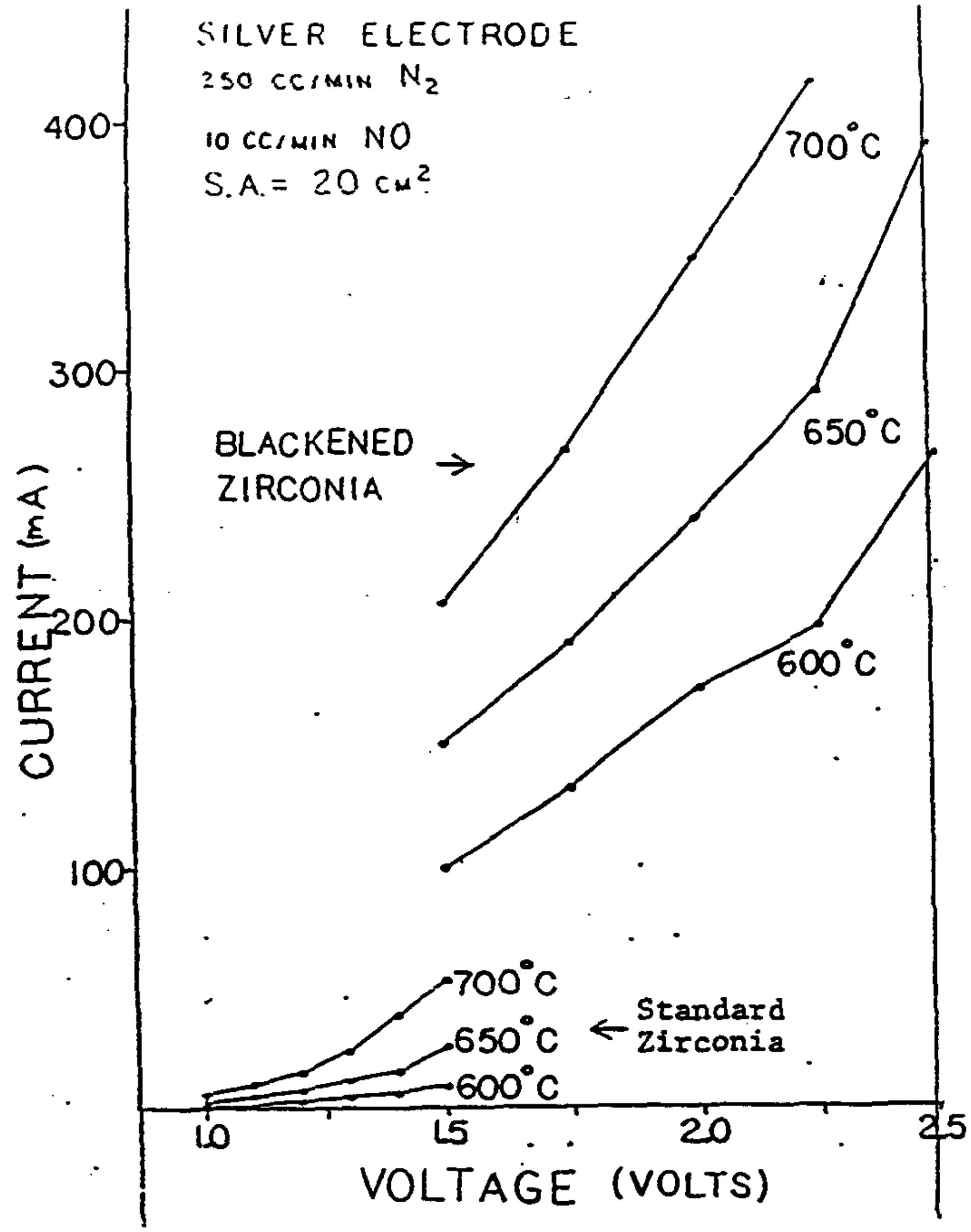


FIGURE 4-4. Comparison of the rate of decomposition of NO for standard zirconia versus blackened (reduced surface) zirconia.

4.4 Electrode Materials

The optimal design criteria required of electrodes for use in a solid electrolyte cell are[4]:

- o Electronic conduction
- o Chemical compatibility with electrolyte
- o Chemically inert to SO_x, NO_x, O_2, CO_2 and H_2O
- o Acceptable cost/performance
- o Porous or high oxygen ion conductivity
- o Catalytically active.

The following electrodes were evaluated by Ceramatec[4]:

- o Noble Metals: Pt, Au, Ag
- o Semiconductor sulfides: MoS_2, FeS_2
- o Doped Oxide Conductors: $La_{0.84}Sr_{0.16}MnO_3$
$Y_{0.92}Ca_{0.08}CrO_3$
- o Metals: Mo-Mn, Inconnel

Figures 4-5 and 4-6 compare the performance of some of the electrodes identified above. Gold electrodes proved to be the best for SO_2 and NO decomposition. The platinum and silver electrodes used by Ceramatec in their test program proved to be short-lived; sulfidation caused the eventual loss of conductivity. However, in an SO_2-free environment these electrodes performed well for NO reduction.

Use of MoS_2 as an alternative non-noble electrode material showed the following results:

- o MoS_2 worked as well, if not better than the platinum electrode;
- o Operating temperature range must be greater than 600°C with voltages higher than 1v;
- o Use of partially-reduced zirconia significantly improved the performance of the cell;
- o Gold electrode performance was significantly better than that of MoS_2;
- o No data was included regarding the impact of SO_2 on the longevity of the MoS_2 material.

FIGURE 4-5

DECOMPOSITION OF NO USING VARIOUS EXPERIMENTAL ELECTRODES

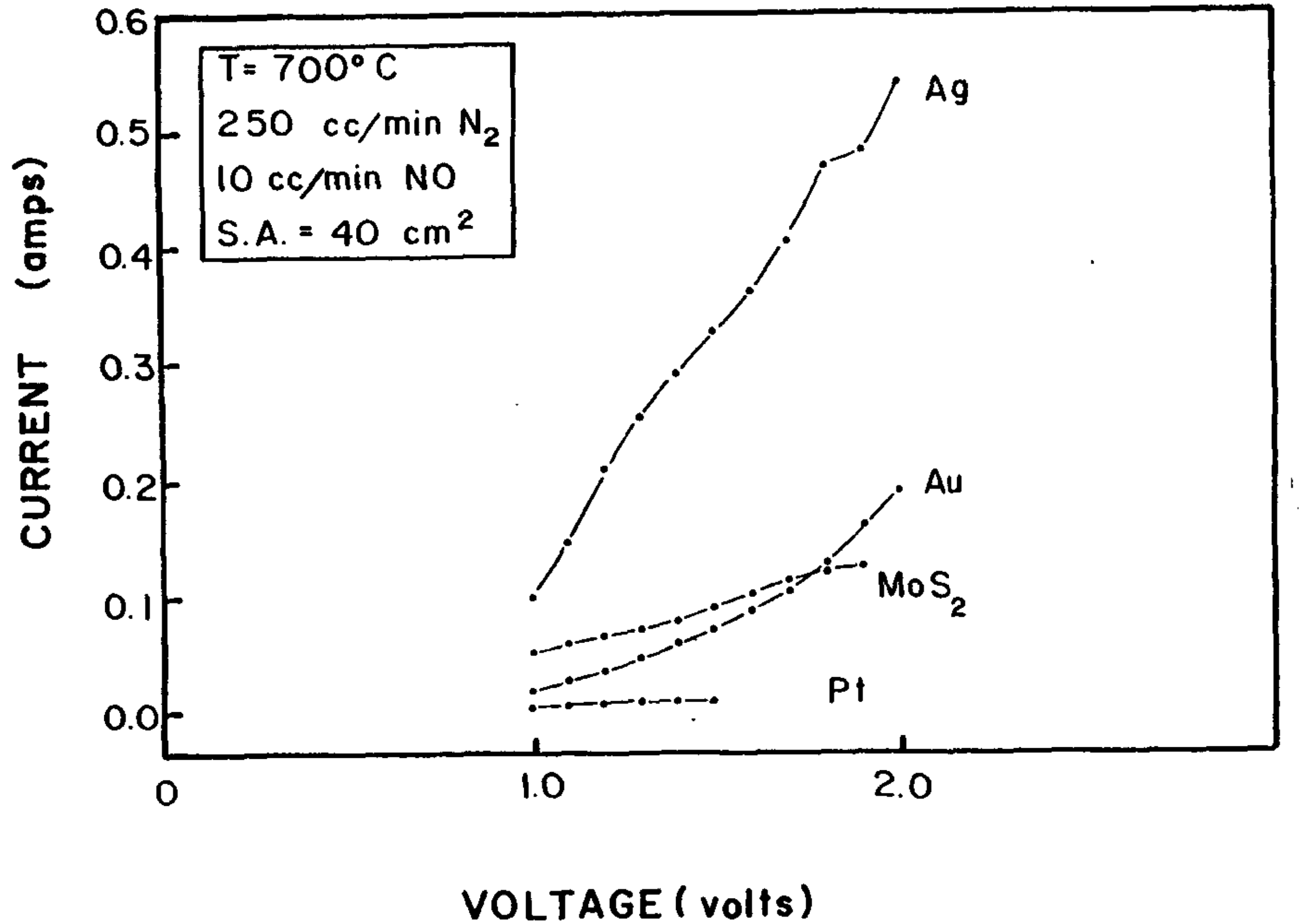
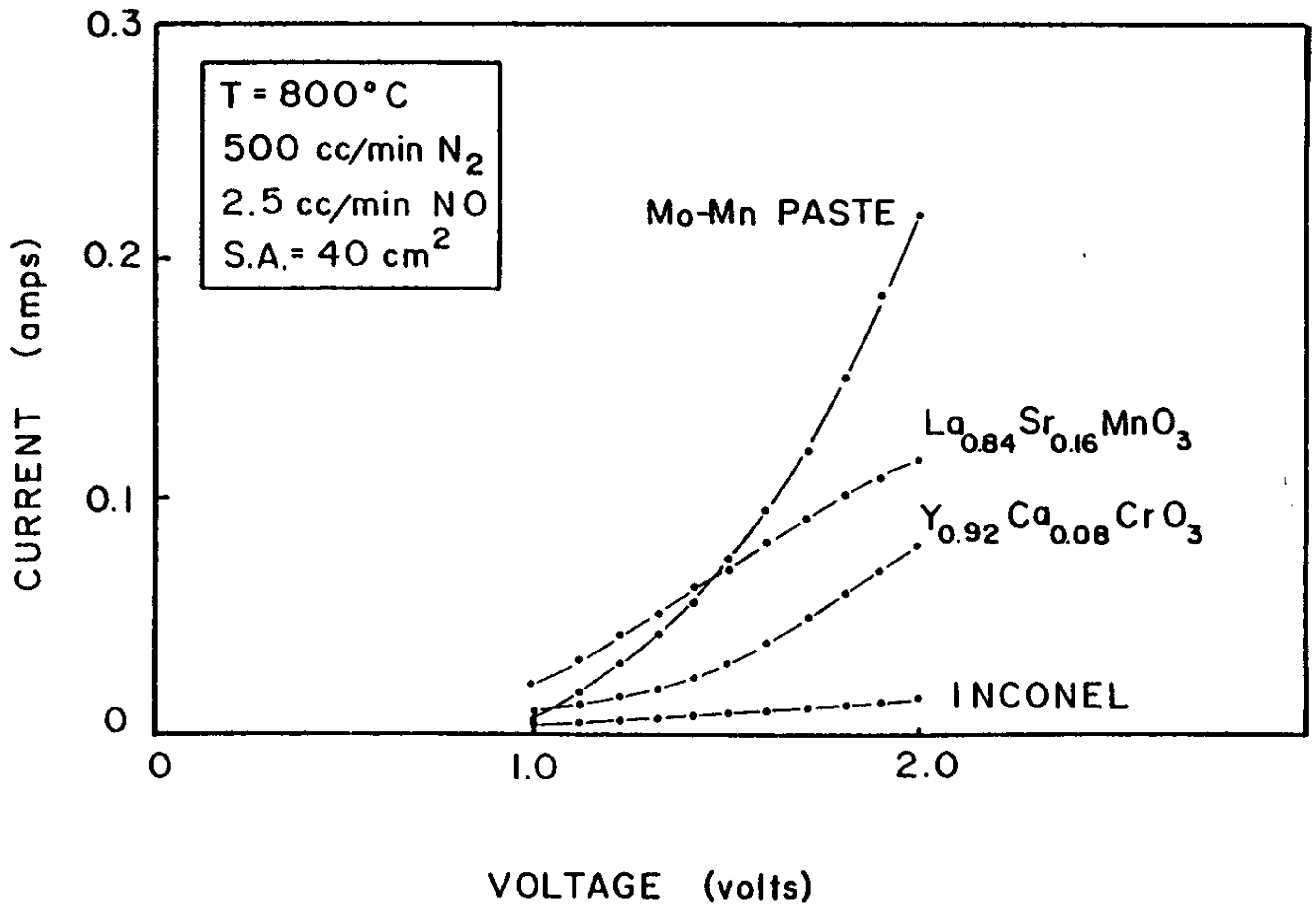


FIGURE 4-6

DECOMPOSITION OF NO USING EXPERIMENTAL ELECTRODES



The gold, FeS_2 and Mo-Mn are the most stable in SO_2 environment.

Development of a long-life electrode for this operating environment is critical to the technology. Ceramatec also recommended the following electrode R&D needs:

- Fabrication procedures have to be developed to optimize gas permeability and adherence of the electrode to the solid electrolyte;
- Electrode resistance to fly ash erosion and degradation by other flue gas impurities must be critically evaluated.

Stanford University research claims that non-noble metals can be used for the electrodes as discussed above.

4.5 Integrated Design Configurations

Preliminary design studies were performed by Ceramatec/VSM (for PETC) for systems applied to 300 lb/hr and 5 tons/hr coal-fired boilers[2], respectively; besides the zirconia cells, key components of this particular design appear to be gas/gas heat exchangers to optimize process heat recovery and sulfur condensation. Since the cell operating temperature was set at 649°C, supplemental flue gas heating is required. Figure 4-7 shows the flow diagram for the Ceramatec/VSM concept. An ASPEN simulation of this design would be of significant help in verifying this work and provide a means of optimizing and developing alternatives; costing on this part of the process could be performed, which would clearly establish the economic goals of the decomposition reactor.

4.6 R&D Considerations

The critical technical issues associated with this advanced technology appear to be as follows:

- There appears to be uncertainty regarding the selectivity of the cell for NO_x reduction as compared with SO_2 and O_2.
- There does not appear to be a clear understanding of the electrocatalytic mechanisms underlying the overall reactions, particularly with electrode blackening; such an understanding is important for design optimization.
- Development of appropriate electrodes with reasonable longevity in the flue gas environment;
- Performance and longevity of alternative electrolytes;
- Impact of fly ash and trace pollutants on the cell operation and lifetime;

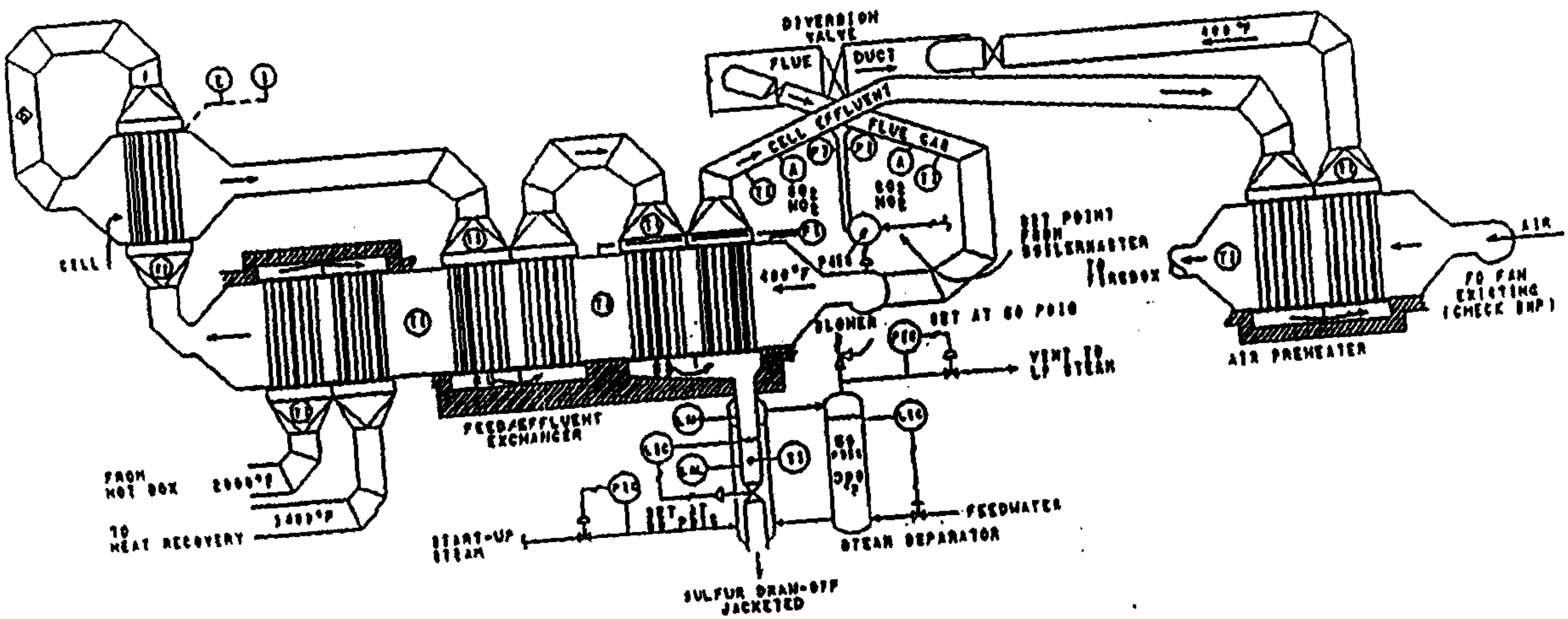


FIGURE 4-7. **Essential elements of a baseline commercial SO_x-NO_x removal system.**
Based on the Ceramatec/VSM design configuration.

- o Viability of geometry and size of the solid electrolyte cell for utility- and industrial-scale flue gas control;
- o Integration of the cell into the power plant cycle, including recovery of sulfur vapor;
- o Process economics compared to commercial processes and other advanced technologies; and
- o Potential for combining this technology with other NO separation technologies, such as NOXSO should be investigated.

This technology has a long way to go to prove itself, but there is considerable potential based on current experimental data.

SECTION 4 - REFERENCES

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5. ELECTRO-CATALYTIC REDUCTION USING INTENSE ELECTRIC FIELDS AND DISCHARGES

5.1 Technology Overview

The only organization currently pursuing this advanced technology concept is the University of New Hampshire. The technology is very early in the development process and all information known at this time is presented in Table 5-1.

TABLE 5-1

TECHNOLOGY NAME: Electro-Catalytic Reduction using Intense Electric Fields and Discharges
TECHNOLOGY TYPE: Direct Reduction to N_2

EMISSIONS CONTROLLED: NO, NO_2, SO_x unknown

TECHNOLOGY DESCRIPTION: Application of high electronic density on a metallic, catalytic surface provides the energy required to excite the NO molecule to the energy level required to dissociate into nitrogen and oxygen. High electron density is potentially achieved by applying high voltage electric fields to electrodes of small dimensions (points or wires) such as metal wool; high velocity electrons travel over the surfaces of the catalyst to contact impacting NO molecules. It is hoped that the subsequent dissociation of NO_x will occur without the addition of chemical reducing agents or the dissociation of other gaseous species.

PREVIOUS PETC EVALUATION UPDATE: 4th Annual Contractor's Conference - U. of New Hampshire (Dept. of Chemical Engineering) Program review, August 1988.

TECHNOLOGY APPLICABILITY: Potentially applicable to flue gas from any combustion source.

DEVELOPMENTAL STATUS: Bench-scale development of this technology for flue gas applications has been sponsored by PETC since May 1987 and will continue until November 1989. Very early in the development of any workable process; PETC expects this initial work to define the technical feasibility and supporting data to establish preliminary process designs and economics.

RAW MATERIALS, UTILITIES: Electricity

BY-PRODUCTS PRODUCED: Elemental nitrogen and oxygen, possibly NO_2, N_2O, elemental sulfur

TECHNOLOGY ADVANTAGES & DISADVANTAGES:

ADVANTAGES	DISADVANTAGES
No reducing agents potentially required	Significant uncertainties at this time
No waste by-products produced	Impacts of exposure to intense electromagnetic fields
Simplistic in concept	Reactor design may be significant problem in terms of electrical control & isolation for DC voltage
High NO_x dissociation has occurred in bench-scale tests	Catalyst longevity in the flue gas environment is a key materials problem; oxidation & sulfidation

TABLE 5-1 (Continued)

TECHNOLOGY NAME: Electro-Catalytic Reduction using Intense Electric Fields and Discharges

CRITICAL DATA GAPS/POORLY UNDERSTOOD PHENOMENA:

Higher voltages and frequencies (above 60 HZ) need to be evaluated to yield higher currents and more energetic electrons.

Alternative electrode configurations need to be evaluated for DC voltage approach. Controlling the electrical breakdown of the glass containment wall has been a major problem.

More realistic flue gas has to be evaluated to establish the impact of combined O_2, H_2O and SO_2. Reduction of SO_2 may result in sulfidation of the metal catalyst. Formation of corrosive H_2S would be quite deleterious. Oxidation of NO to NO_2 and N_2O may occur. Metal catalyst may oxidize and prevent surface current required for NO_x reduction.

Detailed gas analyses must be performed; while on-line NO_x analyzers are sensitive to NO and NO_2, they would not see N_2O.

Capacitor characteristics need to be improved to achieve higher currents for equivalent energy consumption.

As opposed to DC voltage, application of AC voltage results in cyclical currents in the metal catalyst which are strong enough only at the peak of the cycle - this strongly impacts performance. Cycle frequency thus becomes a significant parameter.

RECENT DEVELOPMENTAL ADVANCES:

High electric potential and current flow over the catalytic surface (metal wool) are essential for NO_x reduction.

DC electric fields up to 24 KV applied to metal wool (stainless steel and gold-plated) have shown no NO_x reduction. The key problem here is the breakdown of the air gap between the metal surface and the glass containment, causing arcing and short circuiting. Power consumption is high.

AC electric fields have been shown to operate very favorably with claimed NO conversion of up to 99%, although it has yet to be established that NO was reduced rather than be oxidized to other species such as N_2O.

Upcoming tests will include SO_2 in the simulated flue gas.

KEY TECHNOLOGY SUPPLIERS/R&D ORGANIZATIONS:

University of New Hampshire, Department of Chemical Engineering is performing DOE-sponsored test program. The PI was recently changed from Dr. Arun Someshwar to V.K. Mather, although the former will still provide consultation to the project.

6. ENHANCED DRY SCRUBBING FOR INTEGRATED NO_x CONTROL (Spray Drying and Duct Injection Technologies)

6.1 Technology Overview

Dry scrubbing utilizes an alkaline scrubbing agent which is injected into a spray dryer or ductwork followed by a particulate collection system (baghouse or ESP). The technology was originally intended for the reduction of flue gas SO_2. Spray dryers have been commercial for many years and are predominantly applied to plants burning low-sulfur coals, although good performance for high sulfur coal applications has been obtained. Direct injection of the alkaline sorbent into the flue gas ductwork is a recent development resulting from the desire to provide a low-cost retrofit technology for existing power plants. With increased emphasis also being placed on NO_x control, DOE and others have been sponsoring R&D to develop methods to enhance the dry scrubbing technology so as to simultaneously reduce NO_x. Table 6-1 presents a completed technology data form for enhanced dry scrubbing.

The impetus for this research primarily came as a result of patented work performed by A/S Niro Atomizer in 1983 which modified their spray drying process by the addition of sodium hydroxide[1]. Niro claims that the sodium hydroxide is converted to sodium sulfite (Na_2SO_3) during SO_2 absorption in the spray dryer and uniformly impregnates the spray dried solids and the calcium hydroxide reaction products (some of which are recycled). This solid particulate with active, catalytic sites enters the fabric filter and forms a highly porous filter cake where almost all of the NO_x reduction takes place to yield calcium sulfate, calcium nitrate and calcium hydrogen sulfate-nitrate (Figure 6-1). Niro research shows a temperature "window" in which both SO_2 and NO_x removal are maximized due to the presence of one or two monolayers of water on the sorbent surface in the temperature regime where the process is operated. At temperatures below 195°F, NO_x absorption is claimed to be hindered by too much water, while temperatures above 215°F yield too little water to promote additional SO_2 removal. Niro bench-scale tests achieved a combined removal of 90% SO_2 and 70% NO_x for the following conditions:

- Flue gas O_2 concentration = 5%
- SO_x/NO_x ratio = 1
- Residual moisture present on the spray dried powder
- Large cake build-up in fabric filter (high pressure drop).

While their initial bench-scale tests did not indicate any influence of NO_x/SO_x ratio on NO_x reduction, subsequent pilot-scale tests confirmed a significant dependency; the higher the ratio, the better the NO_x control. They did not formally quantify any generation of NO_2, but it may have been produced in significant amounts.

TABLE 6-1 [DATE: Sept. 1988]

TECHNOLOGY NAME: Enhanced Spray Drying for NO_x Reduction

TECHNOLOGY TYPE: FGD Retrofit for NO_x Reduction

EMISSIONS CONTROLLED: NO, (SO_2 & SO_3 already controlled), 50% NO_x reduction may be possible for high sulfur case

TECHNOLOGY DESCRIPTION: Conventional lime spray drying FGD is modified by the addition of appropriate additives and operating parameters are changed to promote the simultaneous reduction of flue gas NO_x. A variety of additives have been evaluated, such as NaOH, Na_2SO_3, $CaSO_3$, fly ash, ZnO and NaCl. NaOH has been identified as a key spray dryer additive & operating temperature should be greater than 180°F for appreciable NO_x removal; NO_x removal increases with increasing temperature, increasing SO_x/NO_x ratio and inlet oxygen concentration.

PREVIOUS PETC EVALUATION UPDATE: No previous integrated review

TECHNOLOGY APPLICABILITY: Only moderate NO_x reductions are likely and SO_2 removal is compromised by altered operating conditions, unless stoichiometry is adjusted. However, such a technology can be added to the approximately 6100 MW of existing spray dryer capacity and the experience already established with this technology could enhance its acceptance for combined NO_x/SO_x control. Guaranteed performance and economics (and the requirement for NO_x control) will define the market.

DEVELOPMENTAL STATUS: Lime spray drying is fully commercial for low to medium sulfur applications and has achieved high SO_2 removal (>90%) at high sulfur test installations. While the NO_x reduction mechanisms are not understood in the enhanced spray drying process, enough data has been accumulated to implement longer term, large-scale testing with the most appropriate additives.

RAW MATERIALS, UTILITIES: CaO, NaOH, electricity (NaOH-additive process)

BY-PRODUCTS PRODUCED: $CaSO_3$, $CaSO_4$, $Ca(NO_2)_2$, $Ca(NO_3)_2$, Na_2SO_3, Sulfur-Nitrogen compounds

CRITICAL DATA GAPS/POORLY UNDERSTOOD PHENOMENA:

NO_x reaction mechanisms are not well understood.

Operating temperatures above 125°C (225°F) have not been investigated.

Waste by-products have not been fully characterized. Fate of sodium additives has not been detailed.

Additional solids recycle testing should be performed to include some of the by-products produced, such as $CaSO_4$, $Ca(NO_2)_2$ and $Ca(NO_3)_2$.

Very limited large-scale testing has been done (22 MWe ANL plant & Riverside).

TABLE 6-1 (Continued)

TECHNOLOGY NAME: Enhanced Spray Drying for NO_x Reduction (page 2)

TECHNOLOGY ADVANTAGES & DISADVANTAGES:

ADVANTAGES	DISADVANTAGES
Modification of existing FGD technology for combined NO_x reduction	Production of nitrogen compounds (nitrates & nitrites) and nitrogen-sulfur compounds impacts waste disposal options
NO_x reduction is greatest for high sulfur applications - maximizes pollutant reduction potential	Some NO is converted to NO_2 which can yield a visible stack plume, depending on the concentration
Considerable experience has been gained with spray dryer technology	Higher operating temperatures promote NO_x removal, but reduce SO_x removal
No additional major equipment items are required for NO_x reduction	

RECENT DEVELOPMENTAL ADVANCES:

180°F has been verified as the threshold temperature that results in significant NO_x removal and increases with increasing temperature; the removal is enhanced by addition of caustic soda. No optimum temperature has been observed for the simultaneous removal of SO_x and NO_x.

Addition of caustic soda results in a significant increase in fabric filter-cake porosity with more active surface area. Nitrogen oxides removal is proportional to the build-up of the cake on the filter bags. The thicker filter cake provides more active area for oxidation of NO to NO_2. Reaction mechanisms that promote NO_x reduction result in NO_2 production.

NO removal and NO_2 production predominate in the fabric filter rather than the spray dryer (which bodes well for the transfer of this work to duct injection processes).

The most important first-order effects for NO removal in a lime slurry/sodium hydroxide process are:

- Spray dryer outlet temperature; higher the better
- SO_2/NO_x ratio; High SO_x/NO_x ratios are necessary for significant NO_x reduction.
- Flue gas oxygen concentration; O_2 necessary for NO_x control, higher the better

Nitrates and Nitrites appear in the waste products in small amounts at low temperatures; both increase as the outlet temperature of the spray dryer increases. At 210°F (without caustic addition) nitrates increase dramatically, with little addition in nitrites. Greater amounts of calcium sulfate are produced with sodium caustic addition.

TABLE 6-1 (Continued)

TECHNOLOGY NAME: Enhanced Spray Drying for NO_x Reduction (page 3)

RECENT DEVELOPMENTAL ADVANCES: (Continued)

NaCl additive (10 mole %) and a long gas residence time in the spray dryer (30 sec) yielded almost 40% NO_x reduction at low temperature (70°C, 158°F) - residence time influence needs to be further developed.

As temperature is increased to promote NO_x reduction, lime stoichiometries must increase to maintain SO_2 removal which impacts process economics

Solids recycle will play a key role in the enhancement of NO_x reduction; the combination of fly ash, NaOH and $CaSO_3$ have been shown to improve solids reactivity toward NO_x. However, the impact of $CaSO_4$, nitrates and nitrites have not been investigated in controlled experiments.

KEY TECHNOLOGY SUPPLIERS/R&D INVESTIGATORS:

A/S Niro Atomizer:
Patented use of spray drying with NaOH additive

Argonne National Labs:
PETC-sponsored bench-scale parametric tests with various additives, tests with NaOH in ANL's 20 MW spray dryer/fabric filter.

University of Texas:
PETC-sponsored bench-scale parametric tests to evaluate the impact of recycle on combined NO_x/SO_x removal.

Pittsburgh Energy Technology Center:
Parametric tests conducted on 31-inch diameter spray dryer were conducted to evaluate lime/soda ash sorbents for combined NO_x/SO_x removal.

Battelle Memorial Institute:
Patented use of spray dryer with aqueous zinc oxide additive.

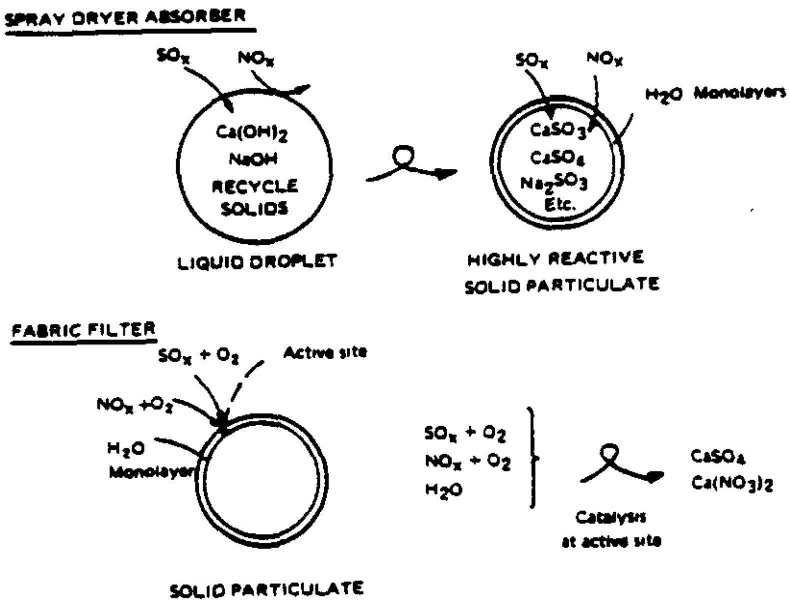

FIGURE 6-1. NIRO PROPOSED REACTION MECHANISM

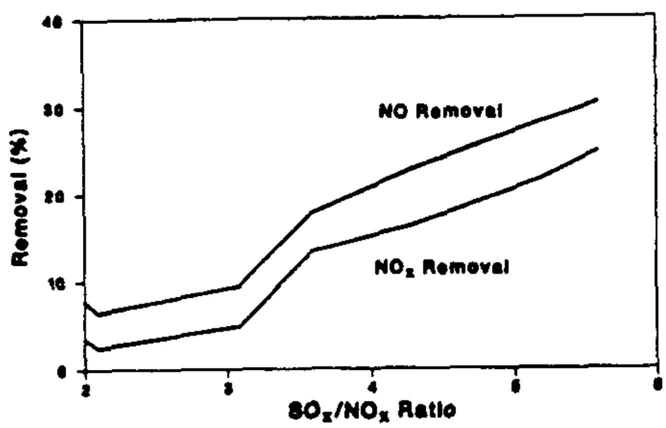

FIGURE 6-2. EFFECT OF SOx/NOx RATIO ON NOx REMOVAL IN ANL'S 20 MW SPRAY DRYER TEST

Subsequent testing at ANL's 20 MW spray dryer, by Niro, yielded 55% NOx and 90%+ SO_2 removal for the following conditions[1]:

- Flue gas O_2 concentration = 6.52%
- SO_x/NO_x ratio = 5.3
- Lime stoichiometry = 1.3
- Filter-cake build-up unknown (pressure drop unknown, but thought to be greater than standard practice).

The chemical composition of the waste product showed the following results which agree with Niro's proposed reaction mechanisms:

- Significant $CaSO_3$ reduction as compared to SO_x removal-only;
- Significant $CaSO_4$ increase;
- Presence of $Ca(NO_3)_2$; and
- Significant yield of Na_2SO_3 (9% by weight).

Over the past 5 years, R&D has been sponsored by DOE and others to confirm the Niro results and to expand the knowledge-base associated with alternative additives and operating parameter inter-dependencies. Table 6-2 lists the key R&D organizations and identifies the thrust of their investigations. The remainder of this section examines the results of this R&D to establish the current technology status and its potential applicability to the duct-injection dry scrubbing alternative.

6.2 Alternative Dry Scrubbing Additives

A significant number of additives have been evaluated to enhance lime-based dry scrubbing systems for NO_x reduction capability[2,3,4,5,6,7,8]. The data presented here may not be complete, but does include the most significant additives tested.

Table 6-3 lists the tested additives, test conditions (if available), additive concentrations, NO_x reduction results and specific comments for each additive type. Based on the various tests performed, the following additives appear to be most promising (with some confusion):

- Sodium Hydroxide (NaOH) - based on ANL, Niro & PETC testing
- Sodium Chloride (NaCl) - based on ANL testing
- Sodium Bisulfite (Na_2HSO_3) - based on ANL testing

TABLE 6-2

RECENT DRY SCRUBBING R&D TO PROMOTE NO_x CONTROL

R&D ORGANIZATIONS	PERIOD OF TESTING	TEST GOALS
Argonne National Labs (Sponsored by DOE)	1985-1988	o Alternative additives[1] o NO_x reduction mechanisms[1] o Alternative FGD chemistries o Parametric testing to optimize emissions control[1] o Large-scale tests[2] o Process economics o Technology transfer - spray drying handbook
Pittsburgh Energy Technology Center	1984-1988	o Alternative sorbents[3] o Parametric tests[3] o NO_x reduction mechanisms
U. of Texas at Austin (Dept. of Chem. Eng.) (Sponsored by DOE)	1986-1987	o Effects of recycle on NO_x/ SO_x removal[1] o Parametric testing of $Ca(OH)_2$/fly ash/$CaSO_3$ sorbents o Parametric testing of $Ca(OH)_2$ /fly ash/NaOH mixtures o Sorbent preparation effects
U. of Tennessee Space Institute (Sponsored by DOE)	1985-1987	o NO_x control potential of lime-based sorbent duct-injection[4] o Physical characterization of spray nozzle/ductwork system o Modeling of droplet motion & evaporation & reaction chemistry
General Electric Environmental Services	1987	o Patented in-duct sorbent injection process for SO_x/NO_x removal[5]
Battelle Columbus Laboratories[6]	1984-1985	o ZnO sorbent tested in bench-scale packed bed with additives

1 Bench-scale, fixed-bed test unit & laboratory spray dryer/fabric filter
2 Argonne's 20 MW spray dryer/fabric filter system
3 PETC 40 SCFM, 31 inch-diameter spray dryer/fabric filter test unit
4 2500 ACFM, 16-inch diameter duct-injection/fabric filter pilot unit
5 50,000 ACFM pilot plant test unit
6 Bench-scale, fixed bed test unit

TABLE 6-3
SUMMARY OF ALTERNATIVE ADDITIVES TESTED FOR LIME-BASED DRY SCRUBBING SYSTEMS

ADDITIVE TYPE	TESTING ORGANIZATION	RANGE OF TEST CONDITIONS	ADDITIVE CONCENTRATION	NO_x REDUCTION RESULTS[2]	KEY PARAMETER DEPENDENCIES[1]	COMMENTS
Sodium Hydroxide	ANL, PETC, U. of Texas, Niro	SO_x/NO_x = 1 - 9 Temp = 150 - 265°F O_2 Conc. = 0 - 11% NO_2 conc. varied Gas humidity varied up to 15%	NaOH Conc.= 0 - 20%	70%+ achieved	Reaction temperature SO_x/NO_x ratio O_2 concentration Gas moisture level Filter cake thickness	Significant interaction between key parameters, Must balance high temp. for NO_x control with SO_2 control requirement, NO_2 production essential for NO removal.
Sodium sulfite (Na_2SO_3)	ANL, Niro, U. of Texas	SO_x/NO_x = 1 - 5 Temp = 150 - 230°F O_2 conc. = 0 - 5.4% NO_2 conc. = 0-50 ppm Gas humidity: 0-15%	0 - 10 mole-%	70% (Niro) NO_2 Increase (ANL)	Reaction temperature SO_x/NO_x ratio O_2 concentration Sorbent moisture level Filter cake thickness	Conflicting results between Niro and ANL data. Niro shows significant NO removal with good SO_2 removal. ANL shows positive NO removal enhancement, but a negative impact on SO_2 removal.
Soda Ash	PETC	SO_x/NO_x = 1.5 - 4 Temp = 170 - 230°F O_2 conc. = 6.5 - 8% NO_x conc. = 500-600 ppm Gas Humidity: 17% CO_2 conc. = 7 - 9% NO_2 conc. = 8 - 64 ppm	9 - 27% by weight	39% achieved	Reaction temperature SO_x/NO_x ratio Soda ash conc.	NO_x removal best 9 wt.% soda ash & 18% hydrated lime @ 210°F. NO_2 generation with increased soda ash & temperature. High SO_x/NO_x ratios increase NO_x removal. Avg. NO_2 conc. increase was 35 ppm.
Sodium bisulfite	ANL	SO_x/NO_x = 5 Temp = 150 - 200°F O_2 conc. = 5.4% NO_2 conc. = 0-50 ppm Gas humidity 7.5-15% by volume	10 mole-%	More than 15% above baseline value	Humidity level (negative impact) Reaction temperature NO_2 level (negative impact)	Significant interaction between key parameters. Must balance high temp. for NO_x control with SO_2 control requirement. More testing required with greater results details.
Aluminum sulfate	ANL	SO_x/NO_x = 5 Temp = 150 - 200°F O_2 conc. = 5.4% NO_2 conc. = 0-50 ppm Gas humidity 7.5-15% by volume	10 mole-%	Less than 5% above baseline value	Humidity level Temperature (negative impact)	Not effective for enhancing NO_x removal.

TABLE 6-3 (Continued)
SUMMARY OF ALTERNATIVE ADDITIVES TESTED FOR LIME-BASED DRY SCRUBBING SYSTEMS

ADDITIVE TYPE	TESTING ORGANIZATION	RANGE OF TEST CONDITIONS	ADDITIVE CONCENTRATION	NO_x REDUCTION RESULTS[2]	KEY PARAMETER DEPENDENCIES[1]	COMMENTS
Fe(II)*EDTA	ANL, Niro	SO_x/NO_x = 5 Temp = 150 - 200°F O_2 conc. = 5.4% NO_2 conc. = 0-50 ppm Gas humidity 7.5-15% by volume	10 mole-%	Less than 5% above baseline value	Temperature (negative impact)	Not effective for enhancing NO_x removal
AL/CIT (complex of aluminum and citric acid)	ANL	SO_x/NO_x = 5 Temp = 150 - 200°F O_2 conc. = 5.4% NO_2 conc. = 0-50 ppm Gas humidity 7.5-15% by volume	10 mole-%	Less than 5% above baseline value	Temperature (strongly neg.)	Not effective for enhancing NO_x removal
NaCl	ANL, Niro	SO_x/NO_x = 5 Temp = 150 - 200°F O_2 conc. = 5.4% NO_2 conc. = 0-50 ppm Gas humidity 7.5-15% by volume	10 mole-%	About 15% above baseline value	Humidity Level (modest)	As effective as NaOH in ANL tests. Parametric testing more limited than with NaOH. More testing required.
CaCl	ANL	SO_x/NO_x = 5 Temp = 150 - 200°F O_2 conc. = 5.4% NO_2 conc. = 0-50 ppm Gas humidity 7.5-15% by volume	10 mole-%	Less than 5% above baseline value	Humidity Level (modest) Temperature NO_2 concentration	Not effective for enhancing NO_x removal.
NaOH/fly ash/ $CaSO_3$ slurry	U. of Texas,	SO_x/NO_x = 0 - 3 Temp = 150-230°F O_2 conc. = 0.5 - 20% Rel. Humidity = 55%	10 mole% NaOH $Ca(OH)_2$/fly ash/ $CaSO_3$ - 1:4:4 wt. ratio	NO_x removal enhanced - no eff. given	SO_x/NO_x ratio Temperature O_2 Conc. Humidity	Effective for enhancing NO_x removal. Combined components reinforce reaction mechanisms. Except for NaOH, other components will not enhance NO_x removal alone.
ZnO	Battelle, PETC			Negligible		Not effective for enhancing NO_x removal.

- Sodium sulfite (Na_2SO_3) - based on Niro testing (ANL tests don't agree)

- Soda ash ($NaHCO_3$) - based on PETC testing.

6.2.1 NaOH Additive Test Results

NaOH has been tested to a much greater degree than the other additives, including several large-scale tests at ANL's 22 MW spray dryer[1,4]. Niro claims to have achieved 70% NO_x reduction at the pilot-level and 55% at the large-scale spray dryer[1]; however, other researchers have not duplicated the very high levels claimed by Niro. PETC and ANL have seen significant increases in the generation of NO_2 concentration under conditions of maximum NO_x removal; a direct relationship has been established between changes in the nitrogen dioxide concentration and nitrogen oxides removal efficiencies. The key parametric dependencies have been shown to be the following (in their order of relative importance):

- <u>Spray dryer outlet temperature</u>

  - Other than Niro, no other researchers have found a temperature window where NO_x & SO_2 removal are optimized

  - ANL has found the critical minimum temperature to be 180°F where NO_x abruptly begins to be removed, even without addition of additives to the lime spray dryer

- <u>SO_2/NO_x ratio</u>

  - Figure 6-2 shows the significant impact of this parameter on NO removal (inlet NO_x concentration is about 500 ppm)

  - High molar ratios of sulfite or bisulfite to NO_x appears to be necessary for NO_x reduction

- <u>Interaction between NaOH concentration and SO_x/NO_x ratio</u>

  - Many significant interactions have been shown to occur between operating variables - ANL's investigations have been most extensive in this regard, but need considerable clarification.

- <u>Inlet O_2 Concentration</u>

  - Oxidation of NO to NO_2 appears to be a key part of the NO_x removal chemistry - higher oxygen concentrations enhance this

Other significant operational impacts associated with the use of the NaOH additive are:

- Almost all of the NO_x removal takes place on the filter cake;
- NaOH partially enhances the removal of NO_x by creating a more porous filter cake with more active surface area;
- The thickness of the filter cake that can be maintained appears to be important to achieve high NO_x reductions (see Figure 6-3 for ANL 22 MW test results). NO_x removal is proportional to the build-up of the cake on the filter - impact on filter pressure drop and the solids handling system are constraints;
- The thicker filter cake provides more active area for oxidation of NO to NO_2. Reaction mechanisms that promote NO_x reduction result in NO_2 production. High concentrations of NO_2 can cause a brown stack plume to occur.
- Nitrates and Nitrites appear in the waste products in small amounts at low temperatures; both increase as the outlet temperature of the spray dryer increases. At 210^oF (without caustic addition) nitrates increase dramatically, with little addition in nitrites. Greater amounts of calcium sulfate are produced with sodium caustic addition (see Figure 6-4 for ANL 22 MW test results);
- As temperature is increased to promote NO_x reduction, lime stoichiometry must increase to maintain SO_2 removal - impacts economics;
- Operating process parameters do not act independently which significantly complicates technical/economic trade-off analyses.

ANL has suggested the following process chemical reactions to explain some of the above results, plus 1) a temperature rise across the fabric filter, 2) increase in nitrates and sulfates in the waste product, 3) problems closing the nitrogen balance:

$$Ca(OH)_2 + SO_2 + H_2O \text{ -------> } CaSO_3 + 2H_2O \quad (1)$$

$$2NO + O_2 \text{ -------> } 2NO_2 \quad (2)$$

$$Ca(OH)_2 + CaSO_3*2H_2O + 2NO + 2NO_2 \text{ ----> } CaSO_4*2H_2O + Ca(NO_3)_2 + N_2 + H_2O \quad (3)$$

$$Ca(OH)_2 + CO_2 \text{ -------> } CaCO_3 + H_2O \quad (4)$$

Using the above reactions, ANL was able to close the nitrogen balance to the 80 - 100% level for the 22 MW testing[4].

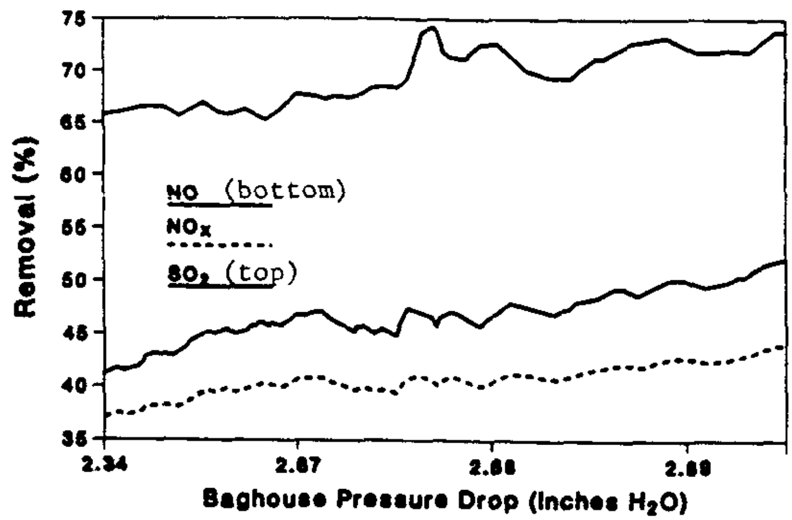

FIGURE 6-3. EFFECT OF BAGHOUSE PRESSURE DROP (CAKE THICKNESS) ON SOX AND NOX REMOVALS IN ANL'S 20 MW SPRAY DRYER TEST

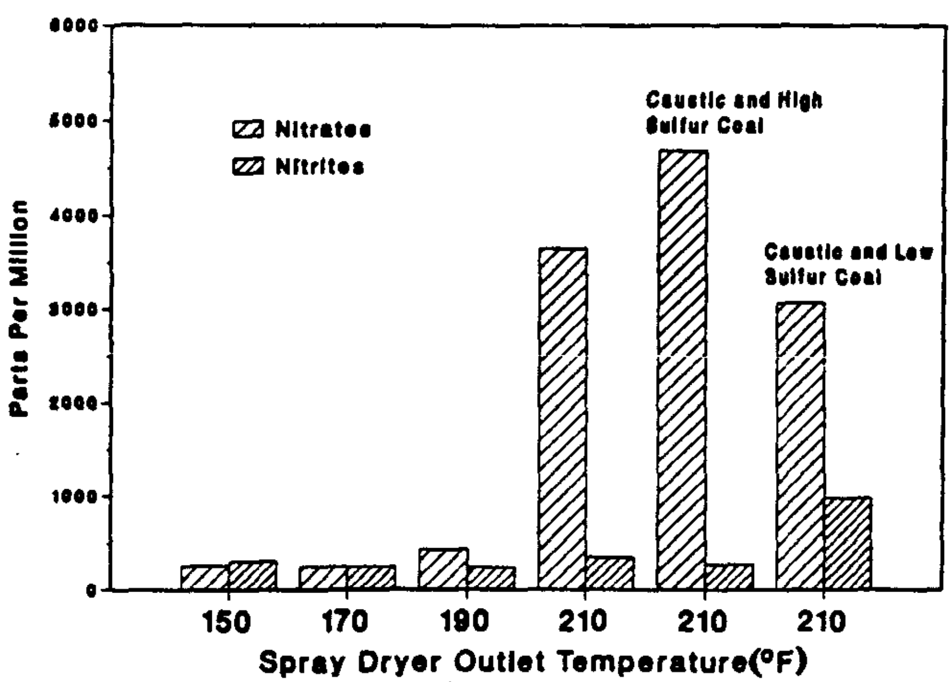

FIGURE 6-4. NITRATES/NITRITES AS A FUNCTION OF CRITICAL PROCESS VARIABLES

6.2.2 NaOH Additive/Fly Ash/$CaSO_3$ - Recycle Evaluation

The University of Texas was sponsored by DOE to perform experimental tests to establish the impact of recycled spray dryer product solids and fly ash on combined NO_x/SO_x removal performance[8]. The tests were conducted at the bench-scale level in a packed bed reactor at bag filter conditions; combinations of $Ca(OH)_2$, fly ash, NaOH and $CaSO_3$ were evaluated. These tests have significant, practical implications based on the need to maximize the utilization of the lime by recycling collected solids. They are also important because the ANL large-scale tests may not be fully representative of potential applications of such a process because the coal burned in the ANL boiler is relatively low ash with low alkalinity[9].

The tests evaluated the effects of temperature, relative humidity, additives (NaOH and Na_2SO_3 and fly ash), and the gas concentrations of SO_2, NO_x and O_2. The key results were reported as follows:

- The most reactive solid for NO_x removal was prepared by slurrying $Ca(OH)_2$ with fly ash, and $CaSO_3$*$0.5H_2O$ in a weight ratio of 1:4:4 with addition of NaOH (10 mol% of $Ca(OH)_2$). Only the 1:4:4 solids ratio was tested.

- The slurry components appear to interact to co-promote the important NO_x reduction mechanisms. NaOH is claimed to play an important role as a deliquescent, a fly ash dissolution enhancer and as a possible catalyst. The fly ash appears to enhance the $Ca(OH)_2$ reactivity - during the recycle the silica and alumina in the fly ash react with the $Ca(OH)_2$ to form a more reactive aluminum-silicate-hydrate which precipitates onto the surface of the fly ash. When slurried with the fly ash and NaOH, $CaSO_3$ significantly improved the solids reactivity toward NO_x, but cannot alone enhance NO_x reduction.

- NO_x removal increases with increasing temperature. No temperature window was found which optimized NO_x and SO_x removal. Higher temperatures negatively impact SO_x removal.

- In agreement with other test data, increased SO_x/NO_x ratios were found to improve NO_x removal.

- As found in other tests, increasing O_2 concentration improves NO_x removal; O_2 is necessary for NO_x reduction to take place.

- Na_2SO_3, as an additive, did not enhance NO_x reduction under the conditions tested. This confirms ANL's results with this additive.

- Alternative loadings of fly ash and $CaSO_3$ were not tested. Other recycle components were not included in the study, such as $CaSO_4$, $Ca(NO_3)_2$ and $Ca(NO_2)_2$. Such tests should be conducted.

6.3 R&D Requirements

The testing of the NaOH additive has reached a milestone point where the existing test data must be further evaluated to develop an appropriate process model which can be used to perform technical design and economic trade-off studies. Test results must be put in a form suitable for continued process development and technology transfer to the environmental control community. If possible, ANL, the organization that has done the significant bulk of the additive testing, must find a means to permit the practical use of their confusing test results which show significant interaction among operating parameters. This kind of follow-through investigation will yield a better chance for technology commercialization.

While alternative additives to NaOH have been investigated and have, apparently, been found to be as effective, a better understanding of their potential is needed. Again ANL staff must find a comprehensible means of relating the key parametric relationships which impact process performance. The potential for combining these other additives with NaOH has not been explored. Pilot-scale testing is required for the key alternative additives, such as NaCl and Na_2HSO_3.

Some of the key data gaps that exist for a NaOH additive process are:

- NO_x reaction mechanisms are not well understood. Additional bench-scale testing may be required to test hypotheses.
- Operating temperatures above 125°C (225°F) have not been fully investigated.
- Waste by-products have not been fully characterized. Fate of sodium additives has not been detailed.
- Additional solids recycle testing should be performed to include some of the by-products produced, such as $CaSO_4$, $Ca(NO_2)_2$ and $Ca(NO_3)_2$.
- Prediction of NO_2 generation and possible control.
- Waste disposal methods have to be evaluated.

Some R&D recommendations that might further enhance NO_x removal are:

- Further non-additive enhancement of the filter cake porosity and thickness could be accomplished by the use of an electrostatic augmented bag filter (ESFF); this could further reduce the bag pressure drop to allow a thicker filter cake. Fly ash pressure drop across an ESFF baghouse is about 50% of the pressure drop across a conventional filter. It would also be interesting to determine if NaOH could be eliminated if porosity enhancement is effective. Of course, if the NaOH is acting as a catalyst for NO to NO_2 conversion then the additive will continue to be required.

- Combined additives, such as NaOH, $Na2HSO_3$ and NaCl, may reinforce different reaction mechanisms so as to further enhance NO_2 removal.

Technology transfer to the duct injection program is hindered by the key requirement of the higher temperatures that favor the NO_x removal mechanisms vs. the lower temperatures and high humidity levels that favor SO_2 removal. Temperature levels called for in the duct injection processes are about 10 - 30°F above saturation temperature (about 120°F); the key threshold temperature for combined NO_x removal is about 180°F. The use of steam to further humidify the flue gas at higher temperatures, plus use of an NaCl additive may provide a means of utilizing higher temperatures for duct injection.

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7. GAS SEPARATION MEMBRANES

7.1 Technology Overview

Gas separation membrane processes utilize the flux that results from two gases at different partial pressures attempting to reach a equilibrium pressure as the driving force for NO_x removal. Table 7-1 presents a completed technology data form for gas separation membranes. In the process, two gases are separated by a semipermeable membrane which is selective for NO_x. The flue gas to be separated is placed on one side of a selective semipermeable membrane. Its pressure is designated as P_f. On the other side of the membrane, the partial pressure of the permeating gas (P_p) is less than that of the feed gas causing the flue gas to flow through the membrane. If the membrane is properly selective, the gas species will flow preferentially through the membrane so that the downstream flow is enriched in this species. The volume rate of flow (V) of species i through the membrane with a thickness of T, surface area A and a permeability Q is given by Equation 7-1:

$$V_i = [Q_i * A * (P_f - P_p) / T] \qquad \text{(Eq. 7-1)}$$

Several types of gas separation membranes may be used in the NO_x removal process. The membranes are classified by the properties of the raw material of the film (such as nonporous polymeric, inorganic and microporous) and by whether they are symmetric or asymmetric. As their names imply, symmetric membranes are the same on both sides while asymmetric membranes use different material on the two surfaces.

Each membrane material has advantages and disadvantages for application in gas separation. Inorganic membranes, such as those having a metal or glass base, have the ability to withstand a large pressure differential due to the strength of the material. However, this type of membrane can only be used as a gas separation membrane at high temperatures ($400^{o}C$-$600^{o}C$)[1]. Microporous membranes may be used to separate gases but their chemical selectivity is poor since they only have the ability to separate gases by molecular size[2]. To improve the permeability and perhaps their selectivity, a liquid can be incorporated in the pores of the microporous membrane. Sometimes a complexing agent is added to the liquid to facilitate transport of a gas by forming a complex with it. This type microporous membrane is called an immobilized liquid membrane. The disadvantage of the liquid enhancement is that the liquid may evaporate and the membrane life may be shortened.

Nonporous polymeric membranes, such as those made of silicon and rubber, can either be in a rubbery or glassy state depending on temperature. In the rubbery state, the membranes permeability to gases depends on the product of the gas solubility and gas diffusion coefficient in the polymer. As a result, high permeability is associated with high diffusion coefficients or high solubilities. Thus, these membranes are limited in their selectivity because of the abundance of gases with high permeability. The limited selectivity of the membranes may be improved

TABLE 7-1 [October 1988]

TECHNOLOGY NAME: Gas Separation Membranes

TECHNOLOGY TYPE: Selective Gas Separation

EMISSIONS CONTROLLED: NO, NO_2, SO_2

TECHNOLOGY DESCRIPTION: Gas separation membrane processes utilize the flux that results from two gases at different partial pressures attempting to reach an equilibrium pressure as the driving force for NO_x removal. In the process, two gases are separated by a semipermeable membrane which is selective for NO_x. Several types of gas separation membranes may be used in the NO_x removal process. The membranes are classified by the properties of the raw material of the film (such as nonporous polymeric, inorganic and microporous) and by whether they are symmetric or asymmetric.

PREVIOUS PETC EVALUATION UPDATE: BRSC/SAIC report to PETC - Assessment of Advanced Control Technologies

TECHNOLOGY APPLICABILITY: All flue gas applications, temperature constraints unknown, secondary reduction process is necessary

DEVELOPMENTAL STATUS: Bench-scale testing performed primarily for SO_2 removal

RAW MATERIALS, UTILITIES: Membrane fluids (replacement depends on stability), power, water, possible membrane replacement

BY-PRODUCTS PRODUCED: Concentrated NO_x and SO_2 & minor amounts of other flue gas constituents,

TECHNOLOGY ADVANTAGES & DISADVANTAGES:

ADVANTAGES	DISADVANTAGES
No reagents or sorbents required	Physical/chemical stability of membranes is unknown
Useful by-products can be produced	Flue gas reheat will be required for low temperature operation
Dry process (water may be required for particulate and temperature control	High particulate control removal efficiency will be required
No secondary pollutants	Power needs for membrane pressure drop could be significant
	Concentrated NO_x effluent must be eliminated or converted

TABLE 7-1 (Continued)

TECHNOLOGY NAME: Gas Separation Membranes

CRITICAL DATA GAPS/POORLY UNDERSTOOD PHENOMENA:

NO_x selectivity vs other gas constituents must be determined for membranes under investigation.

Impact of particulates and the degree of control needed must be learned.

Physical/chemical stability of the membrane supports and fluid must be investigated through long-duration tests.

Operating temperature constraints must be investigated. Current tests have been at relatively low temperatures which would require flue gas reheat for plume buoyancy. Operting at higher temperatures would be better if the gas can be cleaned sufficiently of particulate.

Energy consumption to provide adequate membrane pressure drop is a key operational concern

RECENT DEVELOPMENTAL ADVANCES:

Two membrane technology development projects were sponsored by PETC in 1987-1988; both projects were oriented towards evaluation of certain membrane types for combined SO_x/NO_x selectivity as follows:

- Membrane Technology and Research, Inc.: thin-film, polyamide copolymer supported by a micro-porous support membrane

- Stevens Institute of Technology: Micro-porous hollow fiber contained liquid membrane (HFCLM) using selected membrane liquids.

The work performed by Stevens and MTR has, thus far, not concentrated on NO_x removal and the MTR technology has so far shown only moderate selectivity for NO in the tests completed.

KEY TECHNOLOGY SUPPLIERS:

Membrane Technology and Research, Inc.

Stevens Institute of Technology

by the addition of a plasticizer or modifier in which the desired permeating gas is highly soluble[3].

Asymmetric (composite) membranes enable the engineer to incorporate the more attractive attributes of each material into one membrane. For example a nonporous selective material may be combined with a porous, high strength, nonselective material to form a single membrane that is both highly permeable and selective while having the strength to withstand large pressure differentials.

7.2 Current Membrane R&D

Two membrane technology development projects were sponsored by PETC in 1987-1988; both projects were oriented towards evaluation of certain membrane types for combined SO_x/NO_x selectivity as follows:

- o <u>Membrane Technology and Research, Inc.</u> (April 1987 - April 1988): thin-film, polyamide copolymer supported by a micro-porous support membrane

- o <u>Stevens Institute of Technology</u> (April 1987 -July 1988): Micro-porous hollow fiber contained liquid membrane (HFCLM) using selected membrane liquids.

7.2.1 Membrane Technology and Research - Results[4]

A polyamide copolymer formed into a thin film composite membrane was tested at the bench-scale using a synthetic flue gas at 140°F. The following results were obtained:

- o SO_2 permeation 250 times faster than N_2;

- o SO_2 permeation 10 times faster than CO_2;

- o Only moderate selectivity for NO; and

- o Use of 2,3 dimethylaniline, to facilitate SO_2 transport, was not effective.

7.2.2 Stevens Institute of Technology - Results[5]

This program tested various liquid membranes immobilized in microporous hydrophobic flat supports. The membrane liquids tested were:

- o Water

- o $NaHSO_3$ (1N)

- o Sulfolene (15%) in water

- Sulfolene (7%) in water
- Sulfolane (12%) in water
- Fe^{3+}EDTA in water (0.02M)
- Fe^{2+}EDTA in water (0.02M).

The following permeability test results were based on SO_2 concentrations at 500 ppm, 2250 ppm and 5000 ppm:

	SO_2/CO_2	SO_2/N_2
Water	74 - 176	962 - 3872
$NaHSO_3$ (1N)	99 - 204	1664 - 4950
Fe^{3+}EDTA (0.02M)	64 - 197	1547 - 3450

NO_x permeability for the above liquids has not yet been performed.

A hollow fiber contained liquid membrane was built using 600 fibers of Celgard x-10 (100 micron ID); preliminary application results with synthetic flue gas and water as the membrane liquid yielded 80% SO_2 removal. Future testing calls for obtaining permeability measurements for NO_x and combined NO_x/SO_x.

7.3 Conceptual Process Designs

Three types of gas-separation membrane processes have been proposed for combined SO_2/NO_x removal. Membrane development work for all of the process types needs to be conducted. Because each of these process types could be deployed for NO_x only removal systems (provided the membrane was selective for NO_x), overviews of these systems are presented below.

Figure 7-1[6] depicts a gas separation membrane system that uses a partial vacuum on the permeate side of the membrane. The driving force across the membrane is a total pressure difference that is created in this process by a vacuum pump on the permeate side of the membrane. The process starts with a prescrubber which cools the gas to about 50°C and also removes the particulates. The prescrubbed flue gas then passes to the membrane separator at a pressure a few inches of water above the atmospheric pressure. The SO_2 effluent from the membrane separator is passed to a natural gas based reduction process which generates sulfur. A similar process for NO_x reduction would have to be added or the NO_x could be returned to the boiler for thermal destruction.

Due to the significant pressure drop across the membrane (up to approximately 15 psi), candidate membranes must have appreciable

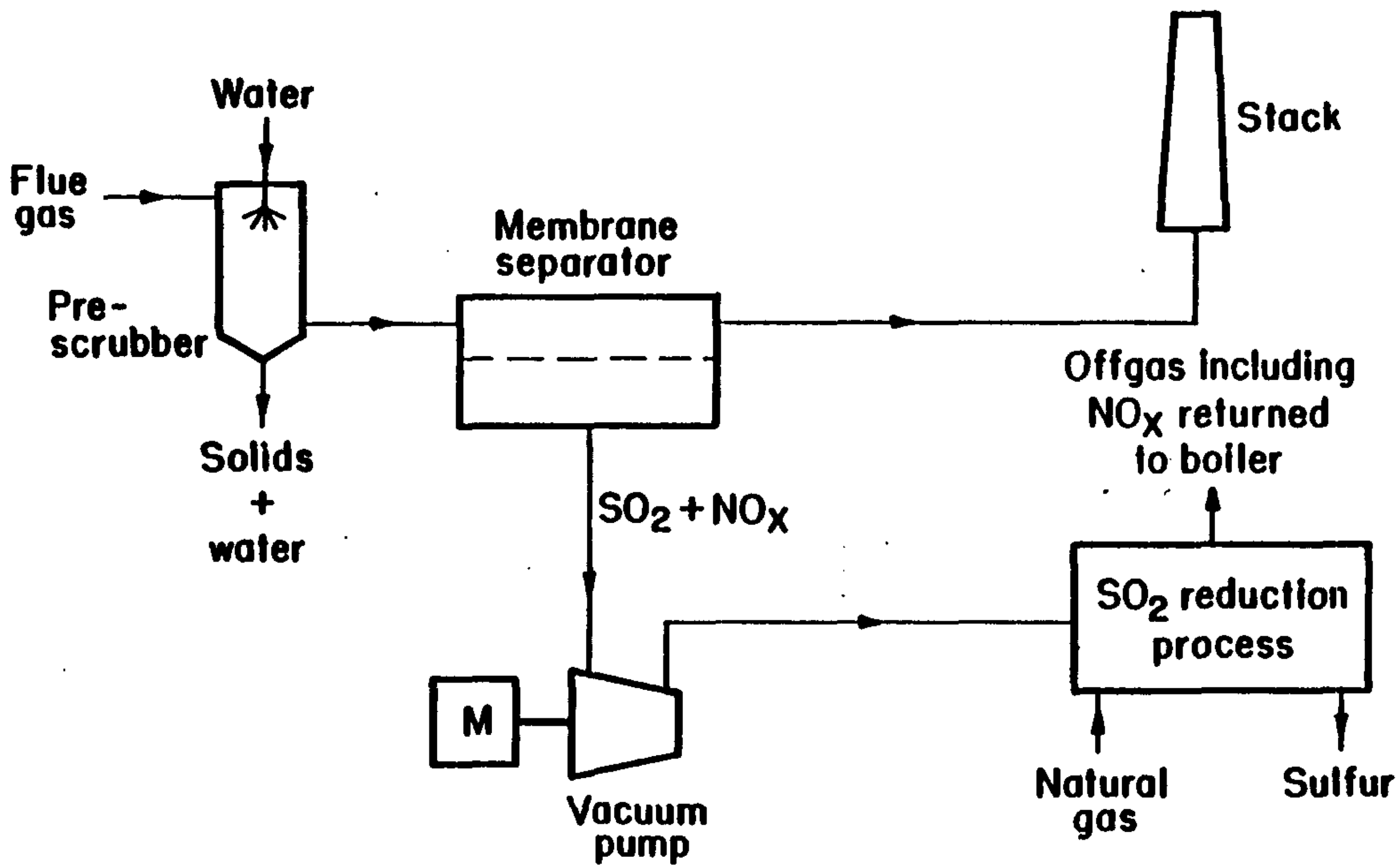

Figure 7-1. Flow Diagram of a Gas Separation Membrane FGC System Using a Partial Vacuum on the Permeate Side of the Membrane

SECTION 7 -REFERENCES

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8. NO_x CONTROL: ADD-ON TO EXISTING WET FGD SYSTEMS

8.1 Background

The potential exists for combining NO_x control with wet FGD process chemistry by adding chelating agents to a scrubbing liquor. This approach to power plant NO_x reduction is particularly appealing to plants with existing FGD systems which may be forced to limit NO_x emissions as a result of future legislation. Utilization of various iron (II) chelates has been researched extensively over the past 15 - 20 years for flue gas applications.

A chelant or chelating agent is a special kind of ligand that contains more than one electron donor group. A ligand is a single compound that can form a complex with a metal ion; ligands usually contain a functional group (an electron donor) with a negative charge or a lone pair of electrons. The formation of a metal-chelant complex (known as a chelate) is thermodynamically favored over a complex formed by ligands containing individual donor groups. The stability of the iron is increased since the ligand keeps the metal from precipitating. The most commonly used chelating agents are aminopolycarboxylic acids, such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and hydroxyethylenediaminetriacetic (HEDTA); their chemical structures are shown in Figure 8-1.

Iron-based chelates have been proven to greatly enhance the solubility of NO in scrubbing liquors via the following reaction:

$$Fe^{2+}(\text{chelate}) + NO \dashrightarrow Fe^{2+}(\text{chelate})(NO) \qquad (1)$$

Once in solution the iron-bound NO readily combines with sulfite to form a variety of products as follows[1]:

$$Fe^{2+}(\text{chelate})(NO) + SO_3^{-} \dashrightarrow aN_2 + bN_2O + cNOSO_3^{=} + dSO_4^{=} + eN\text{-}S \text{ complexes} \qquad (2)$$

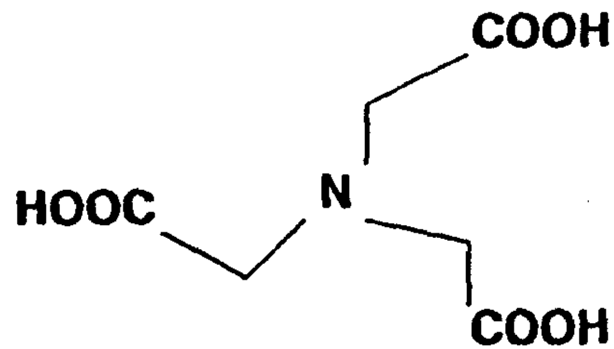
Five key criteria constitute an effective metal chelate[2]:

- o Large absorption capacity for NO;
- o Rapid binding of the NO to form a nitrosyl organometallic adduct;
- o Potential for regenerating the initial complex;
- o Stability of the complex in the presence of typical flue gas constituents; and
- o Ability of the complex to catalytically promote some other NO removal mechanism.

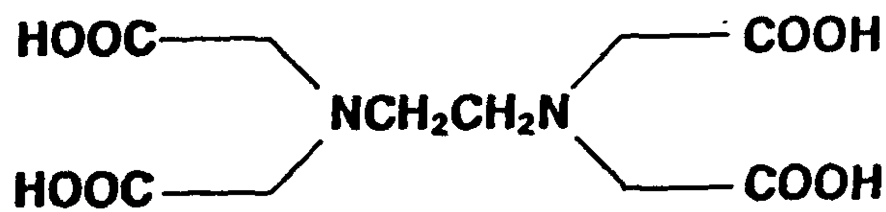
FIGURE 8-1

Common Chelating Agents

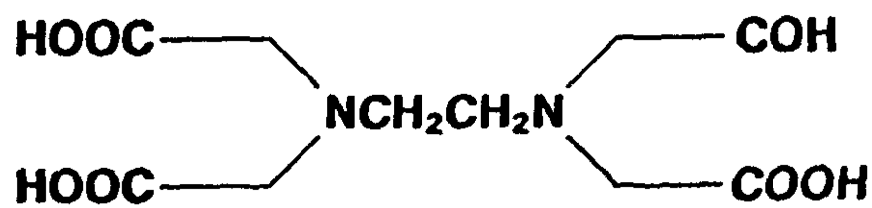
NTA



EDTA



HEDTA



In addition to the above technical criteria, the metal chelates should be adaptable to the lime/limestone and dual-alkali FGD chemistries. Table 8-1 presents the technology review data form for chelate-based, combined NO_x/SO_x FGC technology.

8.2 Japanese Experience

In the 1970's a number of Japanese companies developed wet simultaneous SO_x/NO_x removal processes based on the use of ferrous chelating compounds. These so-called processes have been fully described in a previous BRSC/SAIC report on NO_x control technologies[3]. Most of these processes were based on sodium/calcium dual-alkali process chemistry. By virtue of the NO_x reduction and the formation of various nitrogen-sulfur compounds which must be eliminated, the processes are considerably more complex than the FGD-only processes.

While the SCR technology has dominated NO_x control in Japan since the late 1970's, R&D has continued to examine wet scrubbers for combined NO_x/SO_x control[4,5,6,7,8,9]. This work has focused on the use of the Fe(II)-EDTA/NTA chelating agents to yield an absorption-oxidation process. Reaction mechanisms and kinetics have been studied for sodium-based and magnesium-based scrubber chemistry in order to better understand the process fundamentals. Some of their results are as follows:

- Degree of removal of NO primarily depends on the concentration of Fe(II), which in turn depends on the balance of the rates of oxidation and reduction of Fe. Sulfite concentration should be maintained at 0.2 - 0.25 molar or more.

- The influence of the absorbed SO_2 on NO_x removal only results from the impact on scrubbing liquor pH via the reaction of SO_2 with sulfite.

- Fe(II) is oxidized to Fe(III) by NO in the presence of Na_2SO_3; first order in both Fe(II)EDTA(NO) and Na_2SO_3 and minus first order in Fe(III)EDTA.

- Fe(II) is oxidized to Fe(III) by dissolved oxygen; first order in O_2 and one-half order in Fe(II)EDTA. Excess EDTA helps suppress oxidation.

- The reduction of Fe(III) by sulfite was found to be first order in both Fe(III)EDTA and HSO_3^- and minus first order in Fe(II) EDTA.

- Considerable amounts of N_2O are generated in the pH range of 7 - 10.

- The primary N-S compound produced is hydroxalamine disulfonic acid, $HON(SO_3)_2$.

TABLE 8-1

TECHNOLOGY NAME: Absorption-Reduction Wet FGD/DeNOx

TECHNOLOGY TYPE: NO_x Transformation to Nitrogen/Other Compounds

EMISSIONS CONTROLLED: SO_2, SO_3, NO, NO_2

TECHNOLOGY DESCRIPTION: Iron-based chelates have been proven to greatly enhance the solubility of NO in scrubbing liquors to form a ferrous nitrosyl complex. Once in solution the iron-bound NO readily combines with sulfite (produced by SO_2 absorption) to form a variety of products such as N_2, N_2O, $NOSO_3^-$, $SO_4^=$ and N-S complexes. Chelants, such as NTA, EDTA and HEDTA, tie up Ferrous iron ions in solution so that higher metal and hydroxide concentrations are permitted without metal hydroxide precipitation. Key areas of R&D must deal with oxidation of ferrous chelates to inactive ferric chelates, loss of ferrous chelates from the system, separation of the ferrous chelates from the generated N-S salts which must be purged from the system, and treatment/disposal of the concentrated effluents.

PREVIOUS PETC EVALUATION UPDATE: No previous comprehensive update, contractor project review documents

TECHNOLOGY APPLICABILITY: Applicable to wet, alkaline scrubbing systems which also remove SO_2. Particularly useful for retrofit of existing wet FGD processes for combined SO_2/NO_x control.

DEVELOPMENTAL STATUS: Under development since the mid-seventies by Japanese researchers - focused on using Iron(II)EDTA/NTA. Only pilot-scale systems have been built there. An 800 MW utility installation of absorption-reduction technology in West Germany has failed to meet NO_x control requirements and has been replaced by an SCR system. U.S. researchers have evaluated and characterized a variety of chelating agents and have created promising new ferrous chelates which may significantly simplify the scrubbing/regeneration process. Most work has been performed at the bench-scale. U.S. work has also concentrated on reducing ferric chelate back to the active ferrous form and separating N-S salts from the scrubbing liquor.

RAW MATERIALS, UTILITIES: Ferrous chelate, SO_2 scrubbing agent (e.g. sodium carbonate), steam, electricity, possibly secondary alkaline reagent (e.g. lime)

BY-PRODUCTS PRODUCED: N_2, N_2O, Sulfates, sulfites, nitrogen-sulfur compounds (exact species and their amounts will be process-dependent)

TABLE 8-1 (Continued)

TECHNOLOGY NAME: Absorption-Reduction Wet FGD/DeNOx (Continued)

TECHNOLOGY ADVANTAGES & DISADVANTAGES:

ADVANTAGES	DISADVANTAGES
NO_x control can be added to alkaline scrubbing technology.	Mostly bench-scale-testing has taken place.
Greater than 95% SO_2 removal efficiency due to the larger scrubbing vessel required.	Potentially low superficial gas velocity in scrubber which will yield large absorber vessels.
Can produce potentially marketable by-products (gypsum, sodium sulfate, ammonia sulfate).	Potentially high L/G ratio in scrubber.
Recently developed ferrous chelates may simplify the absorption-reduction process because unwanted N-S complexes may not be formed	Ferrous chelate oxidizes to ferric chelate which requires a reduction step to reverse the reaction.
Electrolytic methods for reducing ferric ions back to ferrous ions may significantly reduce the quantity of iron in the scrubbing solution	High concentrations of iron chelate in the scrubbing liquor will result in high losses in the process purge.
	Nitrogen-sulfur salts and nitrogen-sulfur complexes will be purged-treatment and disposal will be necessary.
	Use for the prevalent limestone scrubbing process may not be attractive.

CRITICAL DATA GAPS/POORLY UNDERSTOOD PHENOMENA:

Thermodynamic and kinetic characterization of the newer classes of ferrous chelates discovered by LBL.

Scale-up of the PETC and Dow Chemical ferric chelate reduction systems.

Further data on ANL's claim that pre-production of the ferrous chelate will result in a more stable additive.

Process design and modelling of various absorption-reduction systems to permit performance and economic assessments, trade-offs, and comparisons.

Treatment/disposal systems for the absorption-reduction process purge stream components.

TABLE 8-1 (Continued)

TECHNOLOGY NAME: Absorption-Reduction Wet FGD/DeNOx (Continued)

RECENT DEVELOPMENTAL ADVANCES:

Fe^{2+}(EDTA)-type metal chelate scrubber chemistry has been fully characterized.

New classes of metal chelates have been discovered by LBL which may create much simpler scrubber chemistry as compared to the conventional iron chelates; the new classes are ferrous thiamino acid complexes, ferrous dithiocarbamates and ferrous xanthates. The main advantage of the latter two types are that they can be produced from relatively inexpensive and abundant raw materials and the reaction products may have potential as agricultural chemicals.
Both PETC and Dow Chemical are advancing the process state-of-the-art by evaluating systems that can alleviate the deficiencies of using the conventional metal chelates. Both organizations are using electrochemical cells, but in different ways.

KEY TECHNOLOGY SUPPLIERS/INVESTIGATORS:

Pittsburgh Energy Technology Center

Dow Chemical USA, Gas/Spec Technology Group

University of California, Lawrence Berkeley Laboratory

Kyoto University, Department of Chemical Engineering

- Dithionate ($S_2O_6^{2-}$) is produced by the reduction of Fe(III) by sulfite, but equilibrates at low concentrations due to oxidation to sulfate.

8.3 Recent U.S. R&D

8.3.1 Argonne National Labs

Under DOE sponsorship, Argonne National Lab (ANL) has evaluated a variety of metal chelate additives for use in both double-alkali and lime/limestone FGD processes[10]. Table 8-2 details the experimental program followed by ANL. The following three metal-chelate complexes were tested extensively:

- Fe(II)-EDTA
- Zinc ethylenediaminetetraacetic acid (Zn-EDTA)
- Ferrous hexamethylenetetramine (Fe(II)-HMTA).

Figure 8-2 indicates that all three metal chelates can maintain 70% NO removal when utilized at a concentration of 0.067 molar in the double alkali chemistry at a pH of about 7. Up to 50% NO reduction was obtained with Fe(II)-EDTA in lime/limestone chemistry.

The following conclusions can be drawn from the ANL R&D:

- Operation near pH of 6.9 shows optimal NO removal, irrespective of scrubber chemistry[2] (see Figure 8-3).
- The primary mechanism for NO_x removal involves the gas-phase formation of N_2O_3 and its subsequent reaction in solution bisulfite to form hydroxylamine disulfonic acid[2].
- Exclusion of oxygen during the preparation of the metal chelate, along with adequate preparation time, yields a stable additive that does not degrade as rapidly as that produced in-situ with oxygen present[11];
- DOWA and citrate chemistries yield relatively poor NO_x removal (less than 50%)[2];
- Iron chelates appear to act in a catalytic manner in promoting the formation of N-S compounds (hydroxylamine-N-sulfonates);
- Addition of Al-Citrate (with Fe(II)*EDTA) can yield over 90% NO removal - Al-Citrate independently promotes the oxidation of NO, while the chelate appears to promote the formation of N-S compounds;

TABLE 8-2

ANL WET SCRUBBER EXPERIMENTAL PROGRAM

Parameter	Values
FGD Chemistries	Lime/Limestone, Double Alkali Citrate, DOWA®
Additives	Fe,Zn / Al,Cu with EDTA / HMTA / Citric Acid
Additive Concentration	0.067 moles/L
Temperature	50°C
Flue-Gas Moisture	7.5% by volume
Flue-Gas Composition (dry basis):	
SO_2	1500 or 3000 ppm
NO	450 or 500 ppm
NO_2	50 or 0 ppm
O_2	5.4%
CO_2	14.5%
N_2	Balance

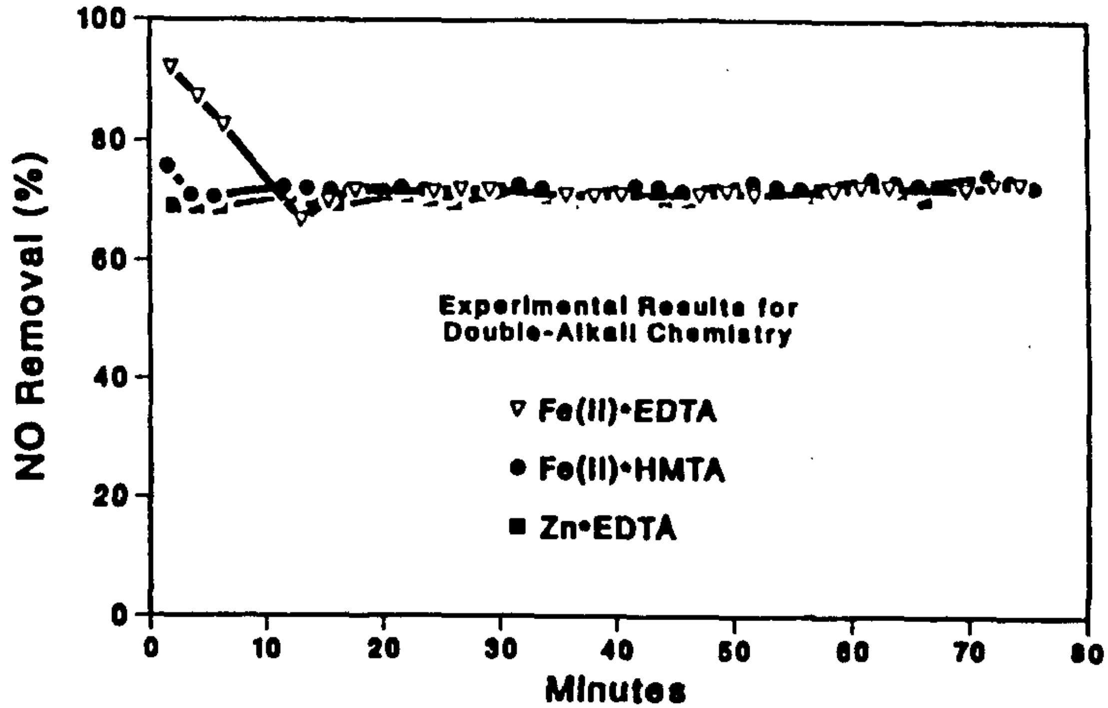


FIGURE 8-2. NITRIC OXIDE REMOVAL IN THE DOUBLE-ALKALI SCRUBBER CHEMISTRY - ANL EXPERIMENTAL DATA

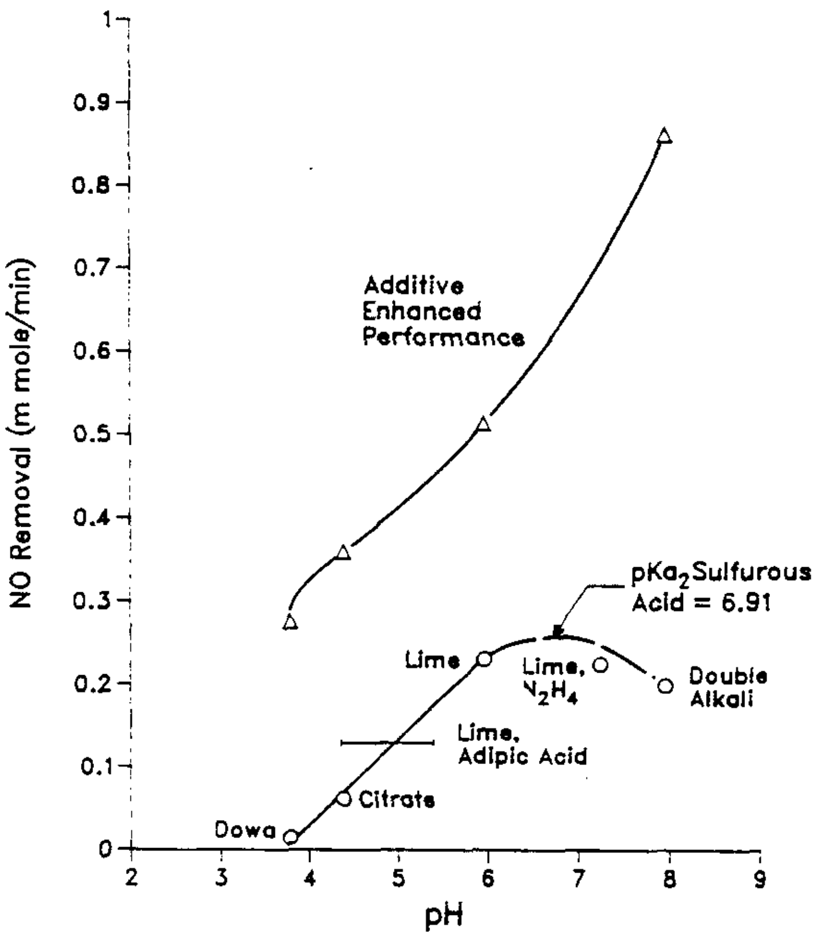


FIGURE 8-3. DEPENDENCE OF NOX/SOX REMOVAL MECHANISM ON PH - ANL DATA

8.3.2 Lawrence Berkeley Laboratory

Since 1982 the Lawrence Berkeley Laboratory has been investigating the thermodynamics, chemical kinetics and reaction mechanisms associated with the use of metal chelates for NO_x removal. The work concentrated on the chemical coordination potential of NO to a number of promising metal chelates and the determination of the products resulting from the reaction of the nitrosyl metal chelates and absorbed SO_2 (in the form of bisulfite and sulfite ions).

The metal chelates tested were:

- $Fe(II)(H_2O)_5$
- Fe(II)(citrate)
- Fe(II)(EDTA), EDTA-ethylenediaminetetra-acetate
- $Fe(II)(acac)_2$, acac-acetylacetonate
- Fe(II)(NTA), NTA-nitrilotriacetic acid
- Fe(II)(oxal), oxal-oxalate
- Fe(II)(citrate)(IDA), IDA-iminodiacetate
- Fe(II)(IDA)
- Fe(II) Chelex 100

Table 8-3 presents some of the kinetic and thermodynamic data associated with the coordination of NO to the above iron chelates.

Some of the key results are:

- The presence of the iron chelate increases NO solubility by a factor of 30000 or more.
- Fe(II)(EDTA) and Fe(II)(NTA) have much larger absorption capacities for NO than $Fe(II)(H_2O)_5$, Fe(II)(citrate) and $Fe(II)(acetylacetonate)_2$[12].
- Upon formation of both nitrous acid (HNO_2) and sulfurous acid (HSO_3^-) in solution, Chang suggested the muti-path reaction mechanism shown in Figure 8-4[12]. After the formation of nitrososulfonic acid(HO_3SNO), the reactions continue along one or more of three reaction paths depending on pH, temperature, and nitrite and sulfite concentration:
    - Additional sulfonation and hydrolysis to form sulfuric acid and reduced nitrogen species; favored by neutral or

TABLE 8-3

KINETIC AND THERMODYNAMIC DATA FOR REVERSIBLE NO COORDINATION TO FERROUS CHELATES

Ferrous Chelates	k_1, mol/(L)	k_{-1}, s^{-1}	K.L/mol at 298 K	$\Delta H°$, kcal/mol	$\Delta S°$, eu
$Fe^{2+}(H_2O)_5(NO)$	$(7.1 \pm 1.0) \times 10^5$	$(1.5 \pm 0.6) \times 10^3$	$(4.7 \pm 2.0) \times 10^{2a}$		
$Fe^{2+}(acac)_2(NO)$	$(4.0 \pm 3.0) \times 10^2$	24 ± 2	17 ± 14		
Fe^{2+}(oxal)(NO)			$\sim 1.0 \times 10^5$		
Fe^{2+}(cit)(NO)			4.9×10^4	- 8.6	- 7.4
Fe^{2+}(cit)(OH^-)(NO)			2.1×10^5	- 3.7	12.0
Fe^{2+}(cit)(IDA)(NO)			$> 3.3 \times 10^5$		
Fe^{2+}(IDA)(NO)			2.1×10^5	- 9.1	- 6.3
Chelex 100(Fe^{2+})(NO)			1.8×10^4	- 7.3	- 5.1
Fe^{2+}(NTA)(NO)	$> 7 \times 10^7$	> 35	2.14×10^6	-11.94	-11.0
Fe^{2+}(EDTA)(NO)	$> 6 \times 10^7$	> 6	1.15×10^7	-15.8	-20.7

where acac = acetylacetone, oxal = oxalate, cit = citrate, IDA = iminodiacetate, NTA = nitrilotriacetate, EDTA = ethylenediaminetetraacetate, and Chelex 100 = a crosslinked polystyrene divinylbenzene porous lattice with attached iminodiacetate multidentate functional groups.

k_1 - Foreward chemical reaction rate constant

k_{-1} - Backward chemical reaction rate constant

K - Chemical reaction rate equilibrium constant

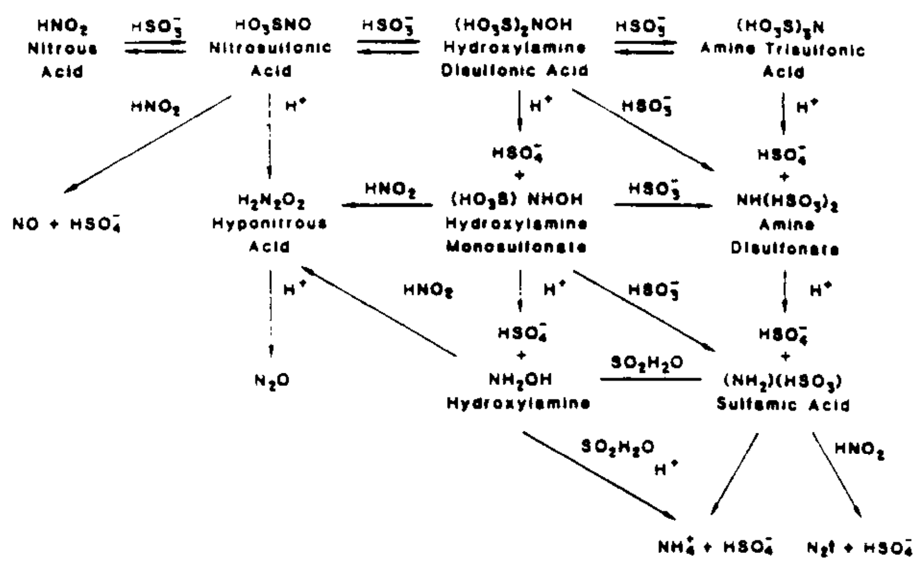


FIGURE 8-4. SUMMARY OF REACTIONS THAT CAN TAKE PLACE AS A RESULT OF INTERACTIONS BETWEEN NITRITE AND BISULFITE IONS. CHANG.

mildly acidic solution. High SO_x/NO_x ratios favor sulfonation products (ATS, ADS and SAM).

- Hydrolysis to form sulfuric acid hyponitrous acid. Low pH conditions (low SO_x/NO_x ratios) favor hydrolysis products (HA, SAM, N_2 and NH_4^+).
- Reaction with nitrous acid to yield sulfuric acid and nitric oxide - favored by lower pH solution.

- Overall reaction rates speed up at higher temperatures.

o Ferrous ions are oxidized to ferric ions (inactive for coordination with NO) in an aqueous system by dissolved oxygen and NO with sulfite. NO removal efficiency cannot be sustained without reduction of the ferric ions.

o Ferric ions are reduced to ferrous ions by sulfurous acid, producing dithionate and a small amount of SO_4^{2-}. The rate of reaction is first order in $[HSO_3^-]$ and $[Fe^{3+}L]$ and inversely first order in $[Fe^{2+}L]$. The rate of formation of the ferric ions is orders of magnitude greater than their reduction. Dithionate is very soluble and cannot be easily removed from a scrubbing solution.

o All of the ferrous nitrosyl chelates studied exist as a mononitrosyl complex.

o In a combined SO_x/NO_x scrubbing process, the nitrogen-sulfur compounds, including the HADS and the amine sulfonates have to be removed from the scrubbing liquors.

o The reduction of ferric chelates to ferrous chelates by H_2S may be a viable method.

During their experimental tests, LBL discovered a new type of ferrous chelate[13,14]; these new chelating agents are cysteine (CyS) and cysteine-derivatives which include acetylcysteine (Accys), penicillamine (Pen), acetylpenicillamine (AcPen), glutathione (GSH) and cysteinylglycine (CyS-Gly). LBL claims that these chelating agents create different and simpler chemistry which produce little or no dithionate or nitrogen-sulfur compounds and that oxidation products can be readily regenerated. The following LBL test results have been obtained:

o NO absorption capacity of ferrous cysteine is slightly higher than that of Fe^{2+}(EDTA).

o The presence of oxygen significantly decreases the NO absorption capacity of all ferrous thioamino acids. Cysteine oxidizes to Cystine (CySSCy) and is catalyzed by the Fe^{2+}.

o Ferrous chelates of N-Acces, Pen, N-AcPen, GSH and cys-gly are more effective at NO removal than that of cysteine.

- o Key factors controlling the absorption of NO by ferrous cysteine (CySH) are: pH, O_2 and SO_2 concentrations in the flue gas, the ratio $[CySH]/[Fe^{2+}]$, and the presence of different additives in the scrubbing liquor.

- o NO removal efficiency of ferrous cysteine with respect to Fe^{2+} can be maximized by using a high $CySH/Fe^{2+}$ ratio and by the addition SO_3^{2-}. The latter ties up oxygen to yield SO_4^- and also reduces cystine back to cysteine.

- o Most of the cysteine is recovered as a combination of CySSCy and $CySHSO_3^-$; these products can be converted back to cysteine (for recycle) by use of H_2S and SO_2 at pH 10 with subsequent neutralization of the reaction mixture to pH 7. Simultaneous application of H_2S and SO_2 resulted in 85% yield of the base CySH @ 60°C regeneration temperature.

- o Ferrous complexes of other SH-containing amino acids and peptides may be more resistant to O_2 and more efficient at absorbing NO than ferrous cysteine.

- o The fate of the absorbed NO was established as follows for the alternative chelates:

Chelate	N_2	N_2O	NO_2^-	NO_3^-
$Fe^{2+}(CyS)_2$	23%	23%	(54% as $Fe(CySSCy)(NO)_2$)	
$Fe^{2+}(Pen)_2$	91%	9%		
$Fe^{2+}(GS)$			85%	5-15%

LBL has also started to evaluate two additional new classes of metal chelates: ferrous dithiocarbamates and ferrous xanthates[15]. Initial NO removal tests of several ferrous dithiocarbamate complexes have shown excellent results with most of the products being N_2 and N_2O in ratios ranging between 4:1 to 10:1. Most of the complexes were most effective under neutral pH conditions, with the exception of $Fe^{2+}(urea\text{-}dtc)_2$ which worked best between pH 9.0 and pH 10.0. Complete characterization of these iron dithiocarbamates is required.

8.3.3 Dow Chemical U.S.A.

The patented Dow NO_x/SO_x removal process makes use of the conventional-type of iron chelates discussed in section 8.1; the process attempts to significantly reduce the total iron concentration of the scrubber solution by maintaining a high concentration of active Fe(II) while alleviating the scrubber solution of the inactive Fe(III) chelate form which results from oxidation by dissolved O_2 and NO[16]. Lower chelate concentrations minimize purge stream losses which contributes to making this type of process uneconomical. Enhanced Fe(III) reduction is accomplished by using an electrolytic cell consisting of cathode and anode compartments separated by membranes. Figure 8-5 shows a simplified schematic of the Dow process.

The scrubbing solution containing both the ferrous and ferric chelates is circulated through the anode compartment; as current is applied to the cell, ferric chelate is reduced in the cathode compartment to the ferrous form and water, the anolyte, is electrolyzed at the anode to oxygen and hydrogen ions. Sodium hydroxide is added to the anolyte solution to neutralize the hydrogen ions. Figure 8-6 presents a schematic of the electrolytic cell.

Both laboratory and field trial tests have been conducted by Dow to characterize the process performance. These tests have yielded the following results:

- NO absorption increases as ferrous concentration increases; increasing Fe(II) concentration above 0.009 M does not significantly increase NO removal. NO removal remains between 70 - 80% as shown in Figure 8-7. These results significantly differ with ANL values.

- Increased steady-state sulfur salts concentration means decreased volume of purge and decreased iron chelate losses[17]; however, NO decreases with increased sulfur salts concentration which means that a performance/cost evaluation is required to determine these process parameters.

- Increased scrubber solution temperature slightly reduces NO absorption.

- Maximum NO removal in lab scrubber was 95%, but enhanced scrubber designs could improve performance beyond this if desired.

- Field tests showed the following reaction products in the scrubber effluent: sulfite, sulfate, thiosulfate, and hydroxylamine disulfonate.

- Electrical current required by the electrolytic cell is determined by the amount of oxidation which occurs in the absorber.

Dow has not addressed the treatment/disposal requirements associated with the nitrogen/sulfur salts purge from the process.

8.3.4 Pittsburgh Energy Technology Center

The Pittsburgh Energy Technology Center (PETC) is conducting R&D on a combined, wet, NO_x/SO_x flue gas cleanup process which also makes use of

FIGURE 8-5

DOW CHEMICAL

Schematic of Field Trial Apparatus

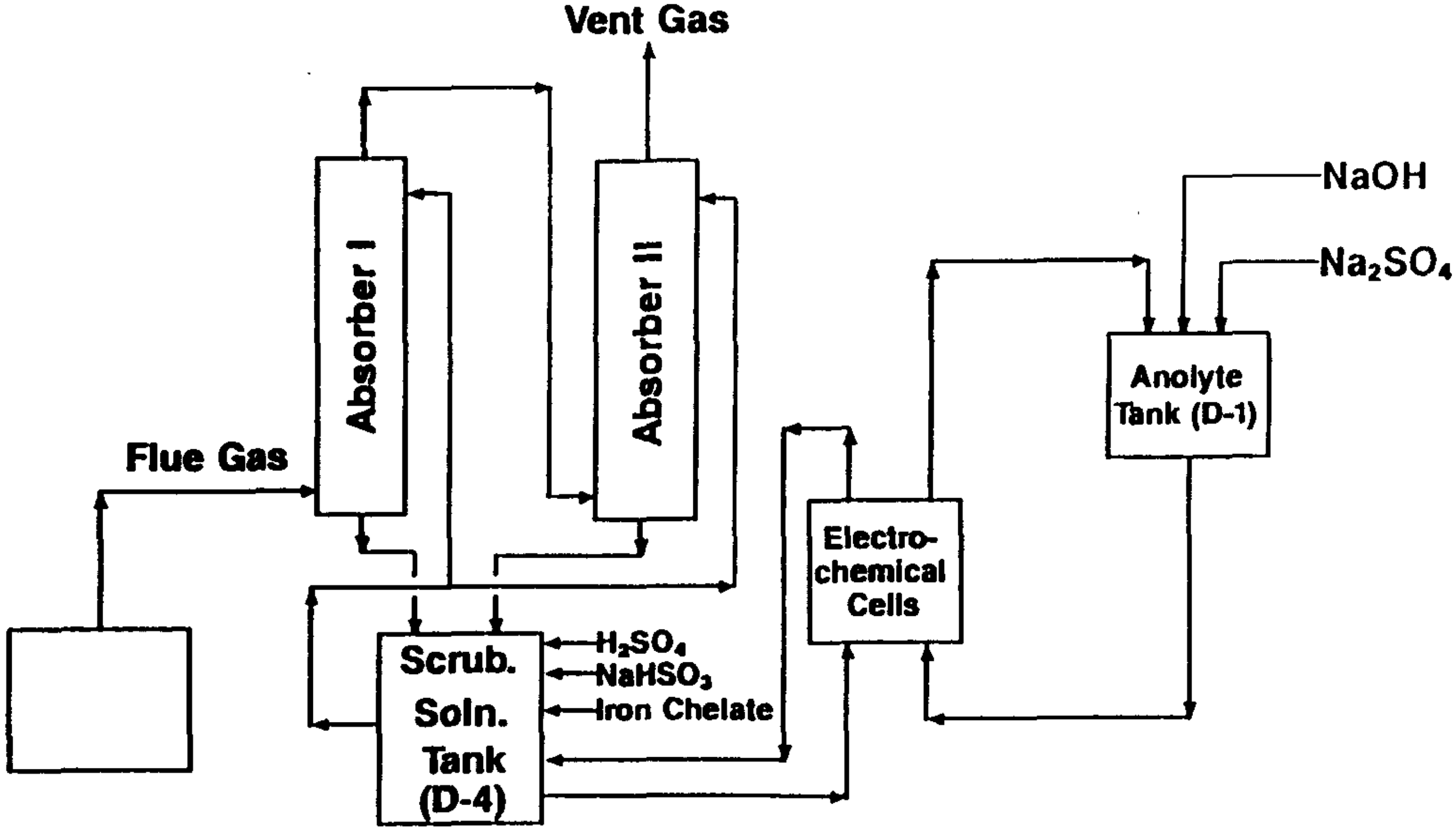
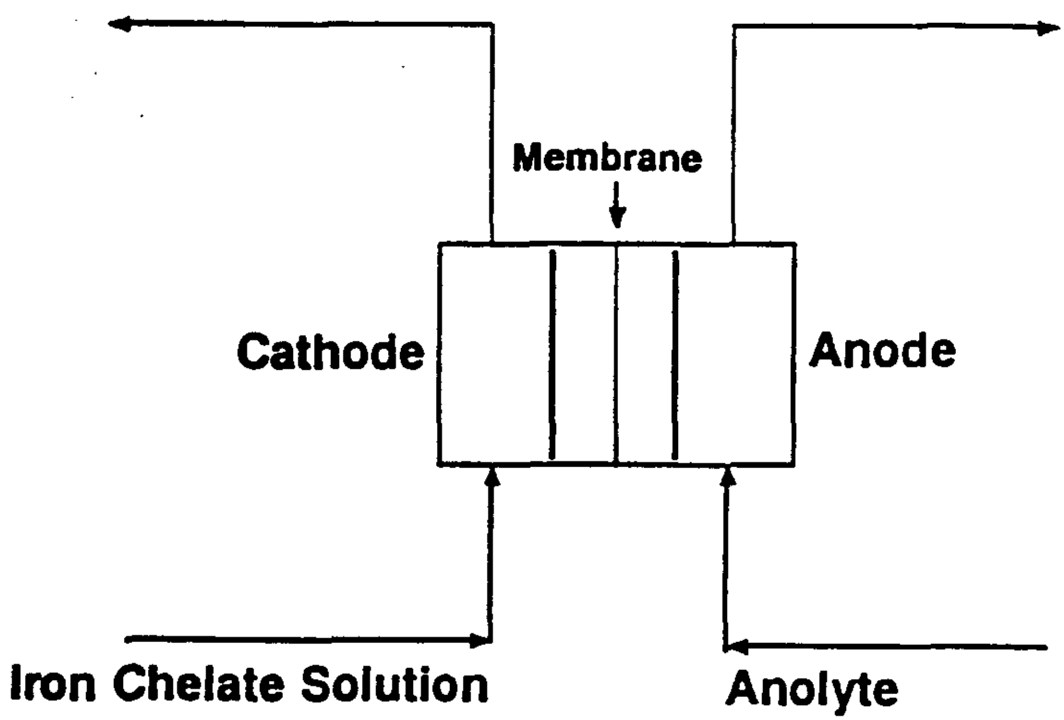


FIGURE 8-6

DOW CHEMICAL

Electrolytic Cell

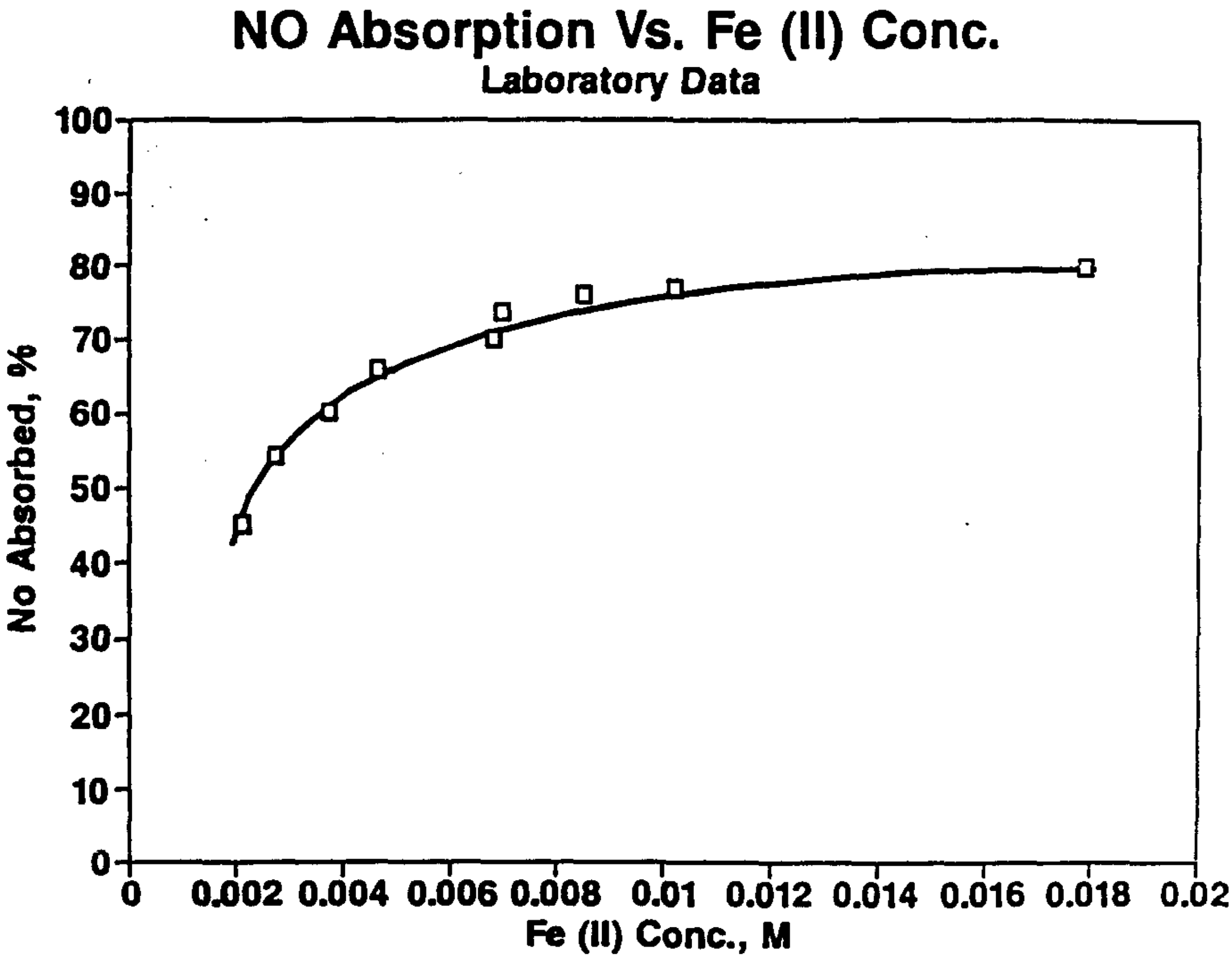


Cathode: $Fe\ (III) + 1\ e^- \longrightarrow Fe\ (II)$

Anode: $1/2\ H_2O \longrightarrow H^+ + 1/4\ O_2 + 1\ e^-$

FIGURE 8-7

DOW CHEMICAL



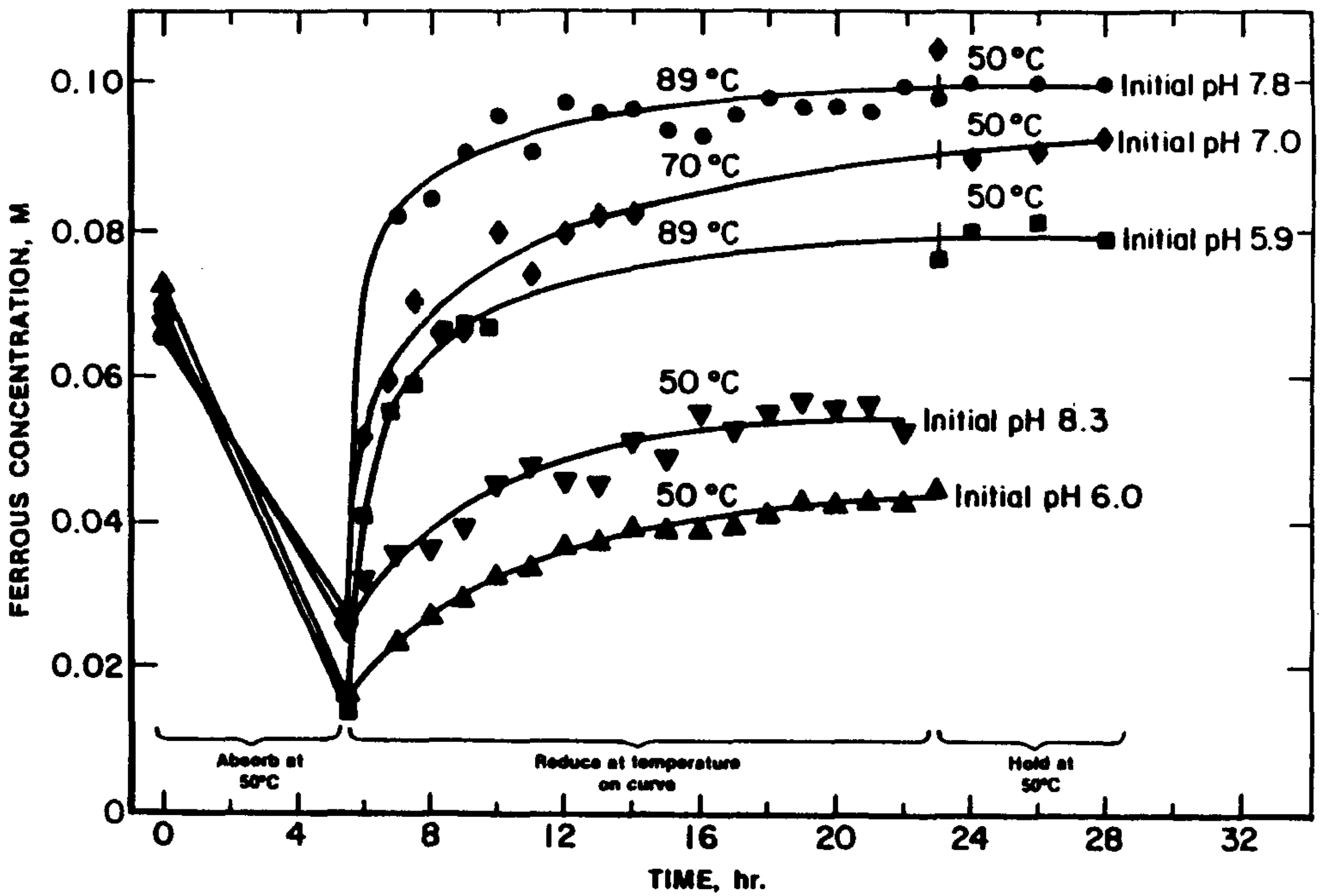


FIGURE 8-8. EFFECT OF INITIAL pH AND REDUCING TEMPERATURE ON FERRIC IRON REDUCTION. PETC DATA.

an iron(II)EDTA chelating agent in combination with sodium-based scrubbing technology[18,19]. The PETC process takes a different approach than Dow in order to minimize chelate losses from the process; a reducing reactor is employed to promote the reduction of ferric ions back to the active ferrous ions by reaction with sulfite to produce sulfate. Figure 8-8 presents experimental regeneration results and the impact of temperature and operating pH. This necessary regeneration process step occurs at approximately 70°C. In order to separate the nitrogen/sulfur salts from the scrubber solution, without losing significant quantities of the chelate, an electrodialysis stack is employed to treat the absorbent flow; the stack uses anion and cation-selective membranes to concentrate the sodium salts and nitrogen-sulfur products. Figure 8-9 shows a schematic of the cell arrangement and the principal transfer of ions, which results in the dilution of sulfite (and other salts and the nitrogen-sulfur compounds) in the diluate compartment and the concentration of sulfite in the concentrate compartment. Potentially, the chelating agent is not transferred, to any significant extent, in the stack and remains mostly in the diluate flow stream. That Fe^{2+}(EDTA) lost in the electrodialysis stack needs to be replaced in the system.

A process flow schematic is shown in Figure 8-10 for a PETC concept that produces sodium sulfate by forced-oxidation of a purge stream of sodium sulfite. Due to greater losses of Fe^{2+}(EDTA) than anticipated, PETC has recently proposed to modify this particular concept by adding lime to precipitate or crystalize gypsum; this dual-alkali approach serves to reutilize the sodium and recover additional EDTA (presuming that it will not be coprecipitated. Further work is required to fully characterize the regeneration step and the electrodialysis system in terms of performance for scale-up and membrane durability.

8.4 R&D Considerations

Over the past 10 to 15 years, considerable experimental research has been devoted to the use of metal chelates in wet scrubbing systems. Recent U.S. work has fully characterized the scrubber chemistry using chelates based on aminopolycarboxylic acids and has also identified new chelates that could significantly reduce the complexity of past process designs.

Based on the increased potential for the passage of some form of acid rain legislation and the likelihood that the clean coal technologies program will set the future direction of future power generation systems, the window of opportunity is occurring now to move ahead with the combined NO_x/SO_x technologies. A three-pronged approach seems logical: 1) provide the opportunity to those companies and institutions who currently have processes at the bench- and pilot-scale to scale-up and test larger, integrated systems; 2)complete necessary thermodynamic and kinetic evaluations (and modeling) of currently known, promising chelating agents within 2 years (the never-ending search for that one perfect sorbent cannot continue forever) and 3) perform the necessary performance/ economic/probabalistic analyses to establish most-likely development pathways. The evaluation studies must begin now and must be performed in a consistent, comprehensive manner based on the available data; the evaluations must take into account treatment and disposal of

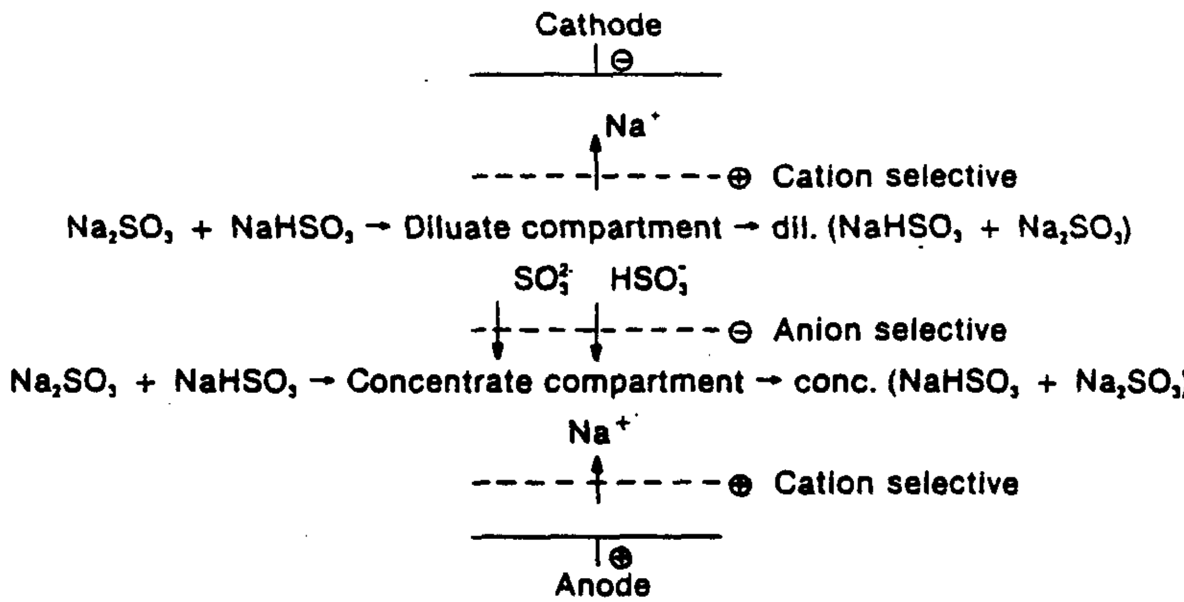


FIGURE 8-9. ELECTRODIALYSIS CELL ARRANGEMENT AND FLOWS FOR NORMAL POLARITY.
(Only one of many stacked cells in the electrodialysis stack is shown).

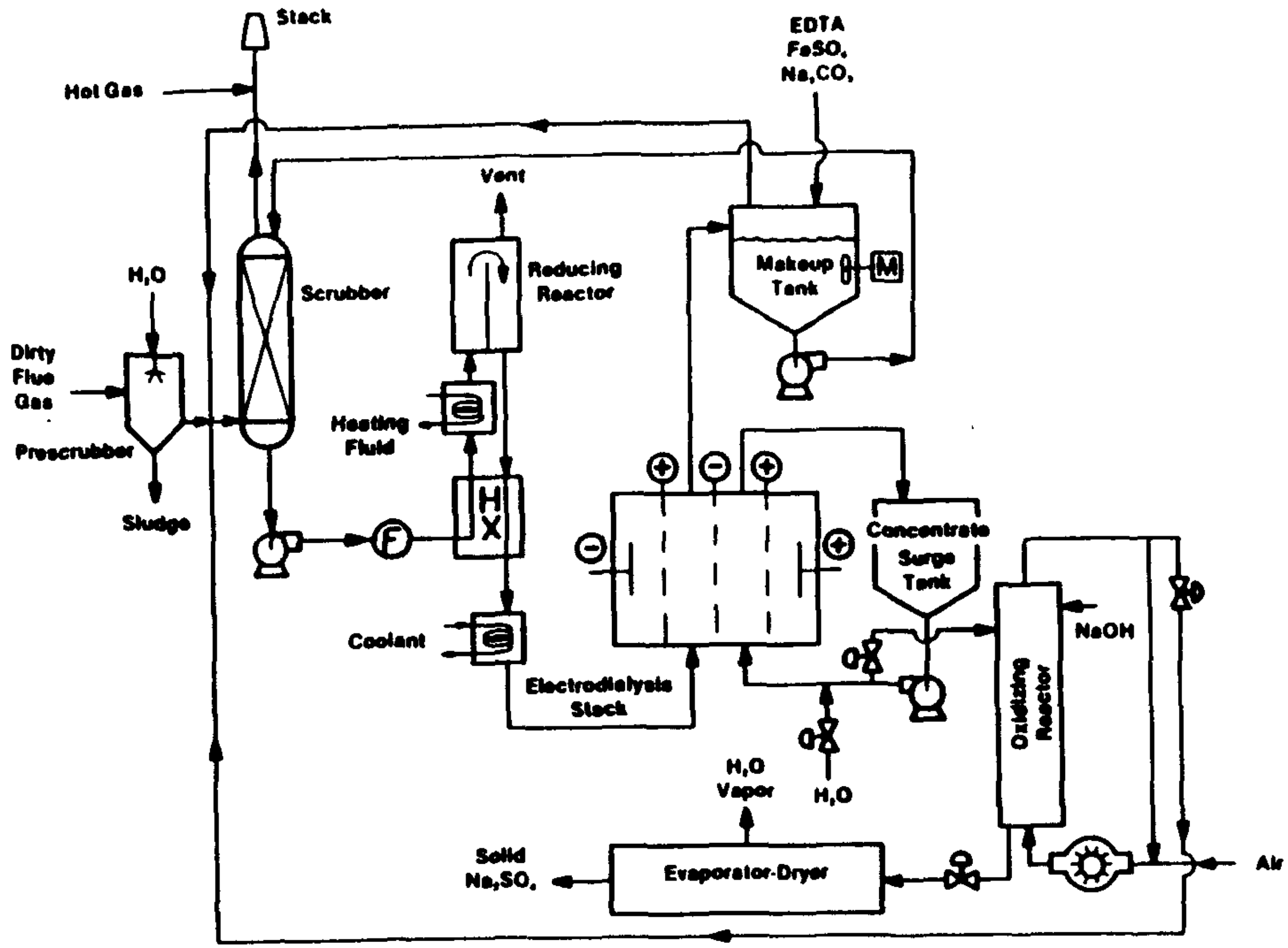


FIGURE 8-10. FLUE GAS CLEANUP PROCESS PRODUCING Na_2SO_4.

effluent streams. Industry must be encouraged to follow-through on the experimental work by showing, if possible, the performance and economic incentives associated with specific processes as compared to alternative technologies.

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